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VOLTAMMETRIC ANALYSIS
OF
SOME GROUP 5 AND 6 TRACE ELEMENTS
IN COPPER

A thesis submitted in fulfilment
of the requirements for the
award of the degree of

DOCTOR OF PHILOSOPHY

from

THE UNIVERSITY OF WOLLONGONG

by

TIMOTHY WILLIAM HAMILTON, BSc(Hons).

806647.

SUMMARY

Two simple methods for the voltammetric analysis of some group 5 and 6 trace elements in electrolytic copper are presented. The described work has application in the local and overseas copper smelting industry.

The first procedure describes the determination of selenium and tellurium in copper. These two elements are first separated from copper by passing an ammoniacal solution of the sample through Chelex 100 resin. Voltammetric interferences from nitrite liberated during the dissolution of the metal sample in nitric acid and from arsenic and antimony present in the metal are eliminated by the addition of hydrogen peroxide. Excess of peroxide is quickly decomposed by the copper (II) ions present. Selenium and tellurium are deposited at the thin gold-film electrode at -0.1 V and analysed by ASV. As little as 0.01 μg Se and 0.02 μg Te per g copper can be determined; relative standard deviations ($n=5$) are in the ranges 1.4-3.7% for selenium concentrations of 7.3-0.6 ppm in copper and 1.6-3.1% for tellurium concentrations of 4.6-0.5 ppm.

The second procedure describes the determination of arsenic and antimony in copper. The copper sample is digested with nitric acid and copper separated from arsenic and antimony by passing an ammoniacal solution of the sample through a column of Chelex 100 resin. After digestion with sulphuric acid and reduction to As(III) and Sb(III) with

sodium sulphite in 7 M sulphuric acid at 80°C, both arsenic and antimony are deposited on the thin gold-film electrode at -0.3 V and, after anodic stripping, antimony is selectively deposited at -0.05 V. As little as 0.06 µg As and 0.03 µg Sb per g copper can be determined; relative standard deviations (n=5) are in the ranges 6.1-15.0% for arsenic concentrations of 5.5-0.5 ppm in copper and 4.1-6.9% for antimony concentrations of 2.6-0.6 ppm.

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Chapter 1

INTRODUCTION

INTRODUCTION

The increase in purity of electrolytic copper during recent years has necessitated a comparable improvement in the means of assessing and controlling quality.

The chemical composition of copper must be regarded as the absolute criterion for quality. Such physical tests as the measurement of electrical conductivity, recrystallisation temperature or spiral-elongation (a method for assessing the softening of copper) may provide circumstantial evidence of a change in the nature of the metal, but only an analysis of impurity content can specifically identify the cause of the change.

There is real difficulty in obtaining sufficiently reliable values for many impurities present in electrolytic copper. For certain elements, an accuracy of the order of 0.1 ppm is needed, whereas in the past a tolerance of 1 ppm or even higher was adequate. Unfortunately, the impurities usually of most concern to the refiner are those, such as selenium, tellurium, arsenic and antimony, which not only require this higher accuracy but are also the most difficult to determine in copper.

The concentrations of impurities in a typical Australian electrolytic (cathode) copper are given in Table 1.

TABLE 1TYPICAL COMPOSITION OF ELECTROLYTIC COPPER (ppm)

Ag	:	2 - 8	Pb	:	<1
As	:	<1	S	:	<1
Bi	:	<0.2	Sb	:	<0.3
Cd	:	<0.1	Se	:	<0.2
Co	:	<0.1	Sn	:	<0.5
Fe	:	<1	Te	:	<0.2
Ni	:	<1	Zn	:	<0.1

EFFECT OF IMPURITIES ON THE PROPERTIES OF ELECTROLYTIC COPPER

Selenium and tellurium are the dominant deleterious impurities in present-day electrolytic copper and two of the most difficult to control and analyse. Tellurium exhibits the greatest unit effect on the recrystallisation temperature of copper, and therefore on its annealability. Next to tellurium, selenium has the most pronounced effect on annealability, although the difference between the coefficients of the two elements is not statistically significant (Reese & Condra 1969). The influence of these two impurities can be traced even when present at levels as low as 0.2 ppm.

Antimony also has an adverse influence, although the unit effect of this element is somewhat lower than selenium and tellurium in softening temperature measurements. Arsenic has only a moderate effect, with the extent of its influence when present in concentrations less than 2 ppm being somewhat obscure. All four impurities significantly reduce the conductivity of copper because they are able to form solid solutions even in the presence of oxygen (Mackay & Armstrong Smith 1966).

Electrical conductivity is an essential property of copper because of its wide use in the electrical industry. The electrical resistivity of a metal is caused by deviations from perfect periodicity of its positive ion lattice. There are several types of lattice imperfections which scatter

electrons and increase resistivity; of these, solute (impurity) atoms have perhaps the largest influence because of lattice distortions caused by ion charge and valency effects. Mott & Jones (1958) have shown that the scattering power of a substitutional solute atom is proportional to the square of the valence difference between the solute and the solvent. Valence difference appears to be a primary reason for the large effect of the group VI (and to a lesser extent group V) atoms on resistivity. Resistivity increases in a linear fashion with impurity concentration for small additions of soluble impurities (Mott & Jones 1958); selenium, tellurium, antimony and arsenic are soluble in copper at the concentrations discussed here.

The *softening temperature* of copper is also affected by the presence of impurities such as selenium, tellurium, arsenic and antimony; the purer the copper the lower is the temperature at which recrystallisation takes place. Lucke & Detert (1957) proposed that the retarding effect is due to preferential solution of the impurity atoms at the boundary between deformed and recrystallised regions. The solute atoms diffuse with the moving boundary until some temperature is reached at which "breakaway" is achieved when the solute atoms can no longer keep up the boundary. Rapid recrystallisation then occurs. As with resistivity, valence and atom size are the most important factors determining the effect of an element on annealability (Bigelow & Chen 1967).

The effect of impurities on the softening temperature

is not linear but rather parabolic or logarithmic; the first ppm of impurity has a much larger effect per atom than further additions (Coutsouradis *et al.* 1974). This nonlinear effect is probably due to positioning of the first few impurity atoms at those lattice sites or imperfections which are most effective in retarding recrystallisation, followed by saturation of these sites and the filling of less effective sites at higher impurity levels (Bigelow & Chen 1967). Finally, the effect of a specific impurity at a given concentration depends on the nature and the amount of the other impurities present.

METHODS OF DETERMINING SELENIUM, TELLURIUM, ARSENIC AND ANTIMONY

A number of instrumental techniques are available for the direct analysis (*i.e.* without resort to separations) of selenium, tellurium, arsenic and antimony in copper, *e.g.* emission spectrometry, atomic absorption spectrometry (AAS), instrumental neutron activation analysis (INAA) and X-ray fluorescence. Here, instrumental methods are defined as those in which modern sophisticated instruments are used for the measurement of that parameter which is indicative of the chemical concentrations to be determined. Gravimetric and titrimetric methods lack sensitivity and are not considered in this review.

At present, *emission spectrography* continues to be the most versatile technique for the analysis of minor constituents in copper, but its limitations in determining trace concentrations of selenium, tellurium, arsenic and antimony are serious; responses (and therefore detection limits) are poor; its degree of reproducibility is only moderate; inter-element effects are present; it needs a series of sophisticated standards; and there is a high contamination hazard. Globule arc-emission spectrography has been used for the analysis of arsenic and antimony in copper and is useful down to a level of 1 - 2 ppm (Burmistrov *et al.* 1976).

The use of direct spectrophotographic methods coupled

with chlorination, iodination and other reactions shows little benefit since the volatility of the copper halides formed is similar to that of the respective halide derivatives of the microimpurities (Elliot *et al.* 1967).

Flame AAS after dissolution and dilution of the copper sample, but without separation of copper from the solution, is limited to impurity concentrations above ca. 100 ppm (Dixon *et al.* 1979) since the spectral lines of copper mask those of the analyte elements. Barnett & McLaughlin (1975) employed flameless atomic absorption spectrometry (FAAS) to extend the limit of detection to 1 ppm for arsenic and antimony. Flameless techniques are limited by copper's moderate volatility, and by masking of the analyte peaks by large non-atomic absorption peaks.

Using *instrumental neutron activation analysis*, Dixon *et al.* (1979) analysed all four elements down to a concentration of 40 ppm. The relatively poor performance of INAA stems from the high activity of the copper-64 isotope and the decay times required for this activity to be sufficiently reduced, as accurate counting measurements then become impossible for short-lived and weak long-lived isotopes. Radiochemical separation is therefore generally necessary.

The need for high dilution factors in preparing dissolved samples for *X-ray fluorescence* severely limits its sensitivity and keeps it out of even the ppm range for most of the elements of interest. The direct analysis of dissolved

copper samples by *spectrophotometric methods* is ruled out by the intense colour that the cupric ion imparts to the solution, and by copper's readiness to complex at least partially with the reagents used. The redox potential of copper, which is electropositive with respect to the elements of interest in virtually all supporting electrolytes, excludes the use of *direct polarographic* and *stripping voltammetric methods* without first separating the analyte impurities from the copper. Such separation appears to be mandatory for the analysis of sub-ppm concentrations of these impurities in copper.

METHODS OF SEPARATION FROM COPPER

The most common method of separating copper from selenium, tellurium, arsenic and antimony is by *coprecipitation* of these elements with a metal hydroxide or hydrated oxide from an ammoniacal solution of the copper sample. Hydrated ferric oxide (ferric hydroxide) is most often reported in this regard (Neiman & Dolgoplova 1975; Mullen 1976, 1977). There is considerable dispute in the literature as to whether recovery of the four elements is quantitative using coprecipitation. Careful control of pH and a strict procedure appear to be essential in obtaining reproducible results. Even so, Se(VI), Te(VI), As(V) & Sb(V) are not quantitatively recovered, so necessitating reduction to the lower positive oxidation states.

Coprecipitation has the advantage that it doubles as a concentration step, with typical concentration factors of 20 to 50. It also has some significant drawbacks: appreciable amounts of Cu(II) are coprecipitated and, along with the metal ion used as the coprecipitating agent, may cause interference problems in the ensuing analysis. The use of Fe(III) gives rise to a bulky amorphous precipitate which is difficult to filter and centrifugation is unwieldy with large sample volumes. The procedure is also fairly lengthy and involves considerable sample manipulation. To reduce the carry-over of copper, more than one coprecipitation is usually needed. Neiman & Trukhacheva (1972)

and Neiman & Dolgoplova (1975) found it necessary to repeat the precipitation three times, thus making the procedure very lengthy and increasing the chance of obtaining low results.

Lanthanum(III) has been used in place of Fe(III) (Reichel & Bleakley 1974) but has the disadvantage that with flameless AAS, a large lanthanum peak is exhibited during atomisation and this interferes with the analysis (Mullen 1976). Among the other coprecipitating agents used with copper solutions are hydrated manganese oxide (Neiman & Sumenkova 1977) and zirconium hydroxide (Adamiec & Marczenko 1975) for the separation of antimony. Arsenic has been used by Luke (1959) and Grunwald *et al.* (1976) for the coprecipitation separation of selenium and tellurium from copper.

Another widely reported method of separating selenium, tellurium, arsenic and antimony from dissolved copper samples is *solvent extraction*. Donaldson (1977) extracted selenium from copper solution as the xanthate, Shimoishi (1975) used 4-nitro-o-phenylenediamine in toluene and Jedrzejewska (1973) used methyl isobutyl ketone to extract tellurium. Arsenic has been extracted with p-xylene (Budesinsky 1979), n-butanol (Pakalns 1969) and benzene (Grimanis & Souliotis 1967). Two drawbacks associated with this method of separation are the co-extraction of small amounts of copper and the limitation of each solvent to the quantitative extraction of only one or, two of the elements of interest. Solvents with a wider range

of applicability invariably co-extract significant amounts of copper and are therefore unsuited to solutions containing copper. In general, extraction separations from copper have been limited to spectrophotometric determinations.

Donaldson (1976, 1977a, 1979) has published separate methods for tellurium, arsenic and antimony which involve coprecipitation with Fe(III) or La(III) hydroxide followed by extraction. Tellurium and antimony were extracted as the xanthate, arsenic as the ethylxanthate. Sufficient amounts of Cu(II) still found their way into the xanthate extract to interfere with most analysis methods. Lanthanum hydroxide coprecipitation has also been used, together with hydride generation, for the separation of selenium, tellurium and arsenic from copper with considerable concentration factors resulting. Because of the severe interference of copper with the reduction of selenium, tellurium, arsenic and antimony to their respective hydrides, it seems impractical to attempt an application of the hydride generation method to the direct separation of these elements from copper solution and no reference to such a method was found.

Antimony has been recovered from copper solution by *distillation* with hydrobromic acid after coprecipitation with hydrous ferric oxide (Van Dyke & Verbeck 1973) and arsenic has been separated by *precipitation* as the element with a mixture of hypophosphorous and hydrochloric acids (Case 1948). The latter method is only applicable to arsenic concentrations greater than ca. 5 ppm in copper. Selenium has been separated

as the *volatile oxide* upon heating the copper sample to 1100°C in a stream of oxygen (Meyer *et al.* 1976), and as the gaseous element from pyrosulphate fusion at 700°C (Kinnunen & Luoma 1978).

No mention of *ion-exchange* separation of impurities from dissolved copper samples was found, although Zelyanskaya *et al.* (1957) reported separating selenium and tellurium from small concentrations of Cu(II) by absorbing the Cu(II) on Espatit KU-1 cation-exchange resin in the hydrogen form; recovery of tellurium was only 70-80%.

In summary then, multiple coprecipitation with Fe(III) or La(III) hydroxide appears to be the only method available for quantitatively separating trace amounts of selenium, tellurium, arsenic and antimony from dissolved copper samples. Because of the drawbacks associated with this method, other methods of separation were explored in an attempt to find a method that was faster and more efficient than the coprecipitation method, and that gave quantitative separation of copper from these elements.

METHODS OF ANALYSIS

The combination of *hydride generation* and *atomic absorption spectrometry* (HGAAS) has become very popular in recent years for the analysis of selenium, tellurium, arsenic and antimony, and it is often difficult to discuss one without involving the other. The combined method consists of reducing the group V and VI elements to their respective hydrides, and venting the gaseous products (including hydrogen produced in the reduction) into a flame or heated tube for the atomic absorption measurement. Sodium borohydride/hydrochloric acid is most commonly used for hydride generation. HGAAS techniques are much more sensitive than direct flame atomisation largely because a high percentage of the analyte metal in from 2 to 100 mL of sample solution can be introduced into the atomiser in a far shorter time than possible if the solution itself were nebulised. (Conventional nebuliser efficiencies are rarely better than 10%).

Using HGAAS with an Ar/H₂ air-entrained flame, detection limits for all four analyte species fall in the range 1-5 ppb in solution (Smith 1975; Nakashima 1979). Flameless HGAAS almost invariably involves the use of a heated quartz tube for atomisation of the gaseous hydrides and exhibits sensitivities which are factors of 3 to 5 greater than the flame technique (Thompson & Thomerson 1974; Evans *et al.* 1979).

Hydride generation is a method involving sudden

mixing of reagent and sample solutions, and because such operations are not very reproducible and because of the number of manual operations involved (the timing of which are rather critical), the precision of measurements is very dependent on the analyst's skill. The efficiency of hydride generation depends on the oxidation state of the element to be reduced, e.g. Se(IV) is reduced far more efficiently than Se(VI) (Pahlavanpour *et al.* 1980), and As(III) more than As(V) (Chan & Vijan 1978). Even so, the generation of hydride from the lower oxidation states is often not quantitative (McDaniel *et al.* 1976; Siemer & Koteel 1977).

Unfortunately, the hydride evolution method is also subject to interference from numerous elements, regardless of the type of finish used (Smith 1975). Cu(II) and Fe(III) in solution cause serious interferences. The causes of interferences in the HGAAS technique are probably manifold but the two most likely to be serious are as follows (Smith 1975): (1) Preferential reduction of the metal ion interference in solution to a different valence state (or to the free metal) can cause precipitation that can either coprecipitate the element of interest, adsorb the volatile hydrides formed, catalytically decompose them, or slow down or completely prevent their evolution from solution. (2) Compound formation can occur in the relatively cool Ar/H₂ flame which explains the mutual interference of virtually all the volatile hydrides with one another. These interference problems have obvious repercussions for the

analysis of copper samples, and this explains why the hydride method is little used for determination of group V and group VI elements in copper.

Flame AAS also presents some problems; the most sensitive resonance lines of selenium, tellurium, arsenic and antimony lie in the far UV region between 190 and 220 nm and this leads to unfavourable signal-to-noise ratios resulting from atmospheric and background absorptions of these spectral lines. Compared with the air-acetylene flame, the argon-hydrogen air-entrained flame leads to greatly reduced flame absorption at these frequencies, but more severe interference effects are observed using the cooler flame (Azad *et al.* 1979). As well, because these elements are relatively volatile, it is difficult to make good hollow-cathode lamps for them.

The increased sensitivity of the *electrothermal* AAS technique is due to the atomic vapour created during the atomisation stage having a much longer residence time in the light beam as compared to the conventional flame method. In this mode, the problem of absorption of source light by the flame is eliminated. However, the excellent absolute sensitivities obtained (Collett *et al.* 1978) become a little less attractive when they are expressed in terms of relative sensitivity, since only 1-50 μL can be analysed. The reproducibility of measurements depends strongly on the sample location within the atomisation chamber, and the performance of the atomiser tube deteriorates continuously,

especially when highly saline samples are analysed. The very small volume in which the vapourised sample is confined (which is the main reason for the excellent sensitivities obtained) results in very high non-specific spectral interferences compared with the flame method. The analysis of selenium, tellurium, arsenic and antimony can be complicated by possible volatility losses during the ashing step and matrix interferences, resulting in poor reproducibility (Chan & Vijan 1978). Both flame and flameless AAS and HGAAS appear to be limited in application to samples which do not contain large amounts of salts or metal ion impurities.

Optical emission spectrometry has also been used in recent years for the determination of selenium, tellurium, arsenic and antimony (Robins & Caruso 1979; Montaser & Mortazavi 1980). Sensitivities for each of the elements of interest are similar to those reported for flameless AAS, but the inductively coupled and microwave-induced plasmas show less detrimental effects due to interferences from compound formation in the flame (Thompson *et al.* 1978). They also afford better precision than flameless AAS techniques, a wider linear calibration range and a simultaneous multi-element capacity (Thompson *et al.* 1978a). However, Cu(II) and Fe(III) seriously interfere, especially with the analysis of selenium and tellurium. Thompson *et al.* (1978) reported that as little as 100 ppb of Cu(II) depressed the tellurium emission signal. One advantage of plasma-emission over flame AAS when using hydride generation is the absence

of interferences due to the various hydrides interacting during atomisation (Thompson *et al.* 1978).

Among the electroanalytical approaches to the determination of selenium, tellurium, arsenic and antimony are polarography, anodic stripping voltammetry (ASV), cathodic stripping voltammetry (CSV) and stripping chronopotentiometry. The main advantages of electroanalytical methods are their great sensitivity (approaching in many cases that of mass spectrometry and neutron activation analysis) and the relatively low instrument and operating costs. In common with most of the other analysis methods (such as HGAAS and spectrophotometric methods) the four elements must be in the lower positive oxidation state. Electrochemical techniques are also ideally suited to solutions with high salt concentrations.

Polarography using d.c. voltage ramps (Buldini 1979) as well as various superimposed voltage waveforms (to minimise non-faradaic currents) have been reported for the analysis of selenium, tellurium, arsenic and antimony. These superimposed waveforms include differential pulse (Henry & Thorpe 1980) and a.c. (Volaire *et al.* 1974). Other polarographic techniques reported include single sweep (Whitnack & Brophy 1969), linear sweep (Volaire *et al.* 1974), cathode ray (Maienthal & Taylor 1965), and the recent application of catalytic hydrogen current to d.c. polarography (Kopanica & Stara 1979). None of these methods, however, are able to determine more than one (or at most two) of the elements of interest in the

one solution, and the presence of Cu(II) interferes with several methods. The sensitivities of these methods appear to extend, for all four elements of interest, down to 1 ppb. The attraction of these techniques lies in their simplicity, speed, relative sensitivity and good reproducibility.

Several of the most sensitive analytical methods for selenium, tellurium, arsenic and antimony have used *anodic or cathodic stripping voltammetry*. The advantages and disadvantages of stripping voltammetry are discussed in the next chapter. Any one ASV or CSV method is generally restricted to the determination of only one or two elements from the group of interest.

A number of electrodes have been used for the ASV determination of these elements including the hanging mercury drop electrode (HMDE) (Kamenev *et al.* 1973), the platinum electrode with codeposition of copper (Araki *et al.* 1973), the gold electrode (Andrews & Johnson 1976), the gold-film electrode (Davis *et al.* 1978), various carbon electrodes (Zakharchuk *et al.* 1975; Topanica & Stara 1978), and carbon electrodes with codeposition of copper (Krapivkina *et al.* 1975), mercury (Neiman & Sumenkova 1976) and cadmium (Neiman *et al.* 1975a). Inter-element compound formation (discussed in Chapter 2) seems to be more of a problem with graphite and mercury electrodes than with electrodes having gold, platinum or copper working surfaces. A wide range of detection limits have been reported for these electrodes, as sensitivity depends on such factors as

deposition time, solution stirring efficiency, the area of the working electrode and the type of waveform used during the stripping step. Limits of detection of ca. 0.03 ppb have been reported for the determination of arsenic and selenium at the gold electrode (Forsberg *et al.* 1975; Andrews & Johnson 1975).

CSV has been reported most often for the analysis of selenium at the HMDE (Forbes & Bound 1977; Forbes *et al.* 1979) with limits of detection down to 0.1 ppb (Shafiqui *et al.* 1976). Antimony has been determined by CSV with a graphite electrode (Brainina *et al.* 1971; Brainina & Tchernyshova 1974) at levels below 1 ppb using its reactions with triphenylmethane dyes

Stripping chronopotentiometry has been used to determine 10 ppb of antimony (Nghie & Vydra 1975). Copper(II) and to a lesser extent Fe(III), posed potential interference problems for many of the electroanalytical methods mentioned. Selenium, tellurium, arsenic and antimony interfere with each other in some of the methods, particularly those using mercury or mercury film electrodes, carbon electrodes, and those involving codeposition with copper.

Spectrophotometric (colorimetric) and fluorimetric methods are widely used for the determination of selenium, tellurium, arsenic and antimony primarily because of their apparent simplicity and low cost. However, these methods are limited in terms of sensitivity, are often lengthy and

tedious, and require a high degree of skill and attention on the part of the analyst to achieve accurate and reproducible results. They are strictly single element methods.

Selenium has been determined recently by fluorimetry with 2,3-diaminonaphthalene (Nazarenko & Kislova 1978), but the method suffers from interference by Cu(II) and Fe(III), and from the instability of the piazsenol which requires that fluorescence measurements be made within 5 min of extraction. Spectrophotometric determination of selenium is carried out most often with 3,3-diaminobenzidine (DAB). The method has been used to determine 1 ppm of selenium in high purity copper (Donaldson 1977), but the analysis is lengthy and DAB has the drawback of being a carcinogen and stringent regulations must be adhered to in order to ensure its safe use. Very wide discrepancies are common between selenium values reported by different laboratories using this method (Mackay & Armstrong Smith 1966).

Tellurium has been determined photometrically as the iodotellurate (Vijayakumar *et al.* 1979), as the hexabromide-diantipyrylmethane (Donaldson 1976) and with bismuthiol II (Cheng 1961). Donaldson's method (1976) for tellurium in copper achieved a limit of detection of 1 ppm. The iodotellurate and bismuthiol II procedures are less sensitive, lack selectivity (particularly with regard to Cu(II) interference) and are restricted because under some conditions the reagents can undergo aerial oxidation to form

products which absorb at the absorption maxima of the tellurium complexes. The sensitivity of the tellurium-diethyldithiocarbamate procedure is very poor.

The molybdenum blue method is widely used for the determination of arsenic in copper (Zot'eva 1973; Donaldson 1977a). Using hydrous ferric oxide coprecipitation followed by extraction of the ethylxanthate complex, Donaldson (1977a) analysed down to 1 ppm arsenic in copper. Silver diethyldithiocarbamate has also been used for the analysis of arsenic in materials used in copper production at levels down to 3 ppm (Budesinsky 1979). Two examining bodies have compared these two methods (A.S.T.M. 1969; Analytical Methods Committee 1975) and have found serious drawbacks with each of them. The molybdenum blue method was considered to have disadvantages in respect of the time required to carry out the determination and the high degree of analytical expertise and the accurate pH control needed to get reproducible and accurate results. With the silver diethyldithiocarbamate method, wide variations between batches of reagents were noticed and copper (II) and nitrate in small concentrations severely interfered with the analysis.

Antimony has been determined photometrically as the iodide (Donaldson 1979), with crystal violet (Adamiec & Marczenko 1975), and with brilliant green (Yadav & Khopkar 1971). Limits of detection lie around 1 ppm after solvent extraction of the complex. Adamiec & Marczenko (1975) used a coprecipitation separation to achieve a limit of detection

of less than 0.1 ppm of antimony in copper. These methods are subject to similar limitations to those already described.

Grunwald *et al.* (1976) have determined down to 1 ppm of tellurium in copper using *X-ray fluorescence* after coprecipitation of tellurium with arsenic; Carvalho & Hercules (1978) used X-ray photoelectron spectroscopy for the analysis of 3 ppb of arsenic in aqueous solution following hydride generation and collection of the hydride by its reaction with mercury to form mercury selenide; and Thompson (1975) has reported the use of *atomic fluorescence* coupled with hydride generation for the analysis of 0.1 ng of selenium, tellurium, arsenic and antimony. In more recent work the atomic fluorescence, Azad *et al.* (1979) and Nakahara *et al.* (1979) report somewhat higher detection limits (about 1 ng) for the analysis of selenium and arsenic respectively.

Gas chromatography has been employed for the determination of selenium, arsenic and antimony. The procedures require the preparation of volatile thermally stable derivatives, and some low limits of detection have been claimed: 0.001 ppm of selenium in copper (Meyer *et al.* 1976) and 1 ppb of arsenic and 10 ppb of antimony in solution (Skogerboe & Bejmuk 1977). When using gas chromatography, losses in accuracy have been observed through molecular rearrangements of derivatives (Talmi & Bostik 1975), and several of the methods are rather time-consuming. *Ion chromatography* has been employed in the analysis of arsenic

in smelter flue dust down to concentrations in the ppb range (Hansen *et al.* 1979).

Finally, *neutron activation analysis* has been reported for the analysis of selenium (Gladney *et al.* 1978), and for the joint determination of arsenic and antimony (Hoede & Van der Sloot 1979; Rengan *et al.* 1979), and selenium, arsenic and antimony (Terada *et al.* 1978). The method exhibits high sensitivity, but it is expensive and analyses typically take a week or more.

The requirements for a satisfactory analytical procedure for these four elements would incorporate a method of quantitatively separating selenium, tellurium, arsenic and antimony from copper followed by analysis of the four elements. The desired limits of detection for all four elements is 0.05 ppm in copper, with relative standard deviations over five determinations of 10% or less at the 0.5 ppm level. The weight of copper required for analysis should be small (ca. 1 g), making the regular analysis of standard samples economically viable. If possible, analysis of all four elements should not take more than one day.

Of the analysis methods discussed, several have been successfully applied to the determination of selenium, tellurium, arsenic and antimony in copper at concentrations down to 1 ppm. Only two methods (AAS and ASV) appear to offer the possibility of determining all four elements at concentration levels of 0.1 ppm or lower. The determination

of selenium, tellurium and arsenic with a limit of detection of 0.05 ppm in copper has been reported by Bedard & Kerbyson (1976), using hydride generation coupled with flame AAS and Neiman & Dolgoplova has claimed detection limits of 0.01 ppm for selenium and tellurium (1975) and 0.05 ppm for antimony in copper (Neiman *et al.* 1970) using ASV.

We chose to investigate ASV in our search for a method for the determination of these elements at levels in copper down to 0.1 ppm on the grounds of the moderate equipment cost involved, and high sensitivity of the technique.

Chapter 2

THE TECHNIQUE OF ANODIC STRIPPING VOLTAMMETRY

INTRODUCTION

Anodic stripping voltammetry (ASV) is a method of analysis based on the more generally applicable, but less sensitive analytical method, polarography (Galus 1976). Use of the method has grown over the past few years because of its ability to simultaneously determine several elements at concentration levels ranging down to the fractional parts per billion with relatively inexpensive instrumentation (Brainina 1974a; Vydra *et al.* 1976). Applications of this technique are reviewed each two years (Kissinger 1974, 1976; Heineman & Kissinger 1978).

Every ASV procedure involves electrodeposition of an element from stirred solution onto a working electrode (e.g. a hanging mercury drop electrode, thin mercury film, or a carbon or metal surface). The metal ions are reduced at the electrode surface at rates determined by their respective concentrations in solution, the applied voltage, the surface area of the electrode, the ionic strength of the electrolyte, and the stirring efficiency. After a short deposition time (typically 1-10 min), the concentration of the metal at the electrode will be some orders of magnitude higher than in the solution.

To strip this material from the electrode, the potential is scanned anodically (towards more positive potentials). As the changing voltage reaches the oxidation potential of each deposited species, the current produced

by its oxidation is recorded and measured. The voltammogram so obtained is a graph of stripping current as a function of the electrode (oxidation) potential. The stripping current due to the oxidation of each element is proportional to the concentration of that element on the electrode (and thus in the sample solution). The height of the current peaks is proportional to the bulk concentration of the element providing the deposition time and the stirring rate are held constant. Although peak height is generally used for convenience, the integrated area under the current potential curve is a more accurate measure of concentration, since it is independent of the shape of the stripping curve and the kinetics of the stripping process. The position of each peak on the potential axis is indicative of the particular element in that electrolyte.

The extremely high sensitivity of ASV is a result of the technique having a built-in separation and concentration step *i.e.* the transfer of the analyte from the test solution to a very small volume electrode. Sensitivity is increased as electrodeposition times are extended. Selectivity can be enhanced by using slower scan rates, accurately controlling the deposition potential, and by judicious choice of electrolyte.

One of the factors that limits the ultimate sensitivity attainable in all electroanalytical techniques is the charging current, *i.e.* the current that flows in the absence of a depolariser, and which is due to changes in the

electrical double layer on the surface of the electrode (Chow 1979). One of the long standing problems in ASV is the separation of this charging (non-faradaic) current from the current due to oxidation or reduction processes (faradaic current).

Modern electronic instrumentation has achieved a measure of separation by applying varying waveforms such as rapid pulse and sinusoidal a.c. to the polarising voltage (Copeland & Skogerboe 1974). The charging and faradaic currents are affected differently by these superimposed waveforms and the charging current can be electronically discriminated and largely removed from the output signal (Rifkin & Evans 1976). This may lead to a considerable gain in sensitivity.

For instance, phase selective a.c. methods involve superimposition of a small amplitude sinusoidal a.c. signal on a d.c. voltage ramp. The faradaic current appears as the in-phase component of the cell current and so can be discriminated and recorded as a function of the d.c. potential (Bond 1975). A similar method is used in differential pulse voltammetry, but instead of a sinusoidal a.c. voltage, a small amplitude voltage pulse is superimposed at frequent intervals on the d.c. ramp, and the cell current is measured at a fixed time after and before the application of each pulse (Flato 1972). Normal pulse voltammetry is somewhat different in that in place of the d.c. ramp, a series of voltage pulses of steadily increasing

amplitude is applied to the cell (Underkofler & Shain 1965).

Another approach to the problem of discriminating faradaic and non-faradaic current is the derivative technique (Hamilton 1976a). The experimental procedure is identical to that of conventional stripping voltammetry, except that the derivative (with respect to time) of the stripping voltage-current curve is recorded. These derivative measurements reflect both the size and shape of the stripping peaks. Perone and Birk (1965) achieved a ten-fold increase in sensitivity for the analysis of Cd(II) by the use of derivative techniques.

ASV generally requires that three electrodes be immersed in the solution: a working electrode, a reference electrode, and an auxiliary electrode. The reference electrode (usually a saturated calomel electrode) has a constant potential (independent of solution conditions) and is used to monitor the potential of the working electrode. The auxiliary electrode serves to complete the electrical circuit with the working electrode and is usually made of platinum. The voltage source used with such an electrode arrangement is called a potentiostat.

Working electrodes used for ASV include the hanging mercury drop electrode (Copeland & Skogerboe 1974), the glassy carbon electrode (Vydra 1976a), various carbon and carbon-paste electrodes (Stulikova & Stulik 1974; Clem & Sciamanna 1975), solid metal electrodes (Adams 1962, 1969),

and thin metal-film electrodes (Stulikova 1973; Stojek *et al.* 1976). The metal-film electrodes, such as the thin gold-film electrode used in this work, consist most commonly of a metal film deposited onto a carbon (or glassy carbon) electrode.

Oxygen may interfere with the reactions at the working electrode by being itself reduced during the determination or by adversely affecting electrode reactions. Air is normally eliminated from solutions during analysis by saturating the solution with an inert gas such as nitrogen.

THE ELECTRODEPOSITION PROCESS

The electrodeposition of trace elements onto the working electrode is influenced by a number of factors:

(a) *Choice of deposition potential.* In most cases, the choice of deposition potential (E_d) is simple; a potential 0.2 to 0.3 V cathodic of the stripping potential suffices. But the irreversibility of some reactions, particularly at metal or metal-film electrodes where the deposited element may bond with the electrode material, may necessitate a more negative E_d than expected. For example, at the gold electrode, elemental selenium is oxidised to Se(IV) at +0.9 V, but Se(IV) is reduced to the element only at potentials cathodic of +0.2 V. When developing new analytical methods, the choice of E_d should be weighed against the requirement of maximising the deposition rate on the one hand, and the possibility of reducing interfering species on the other.

(b) *Deposition time.* The amount of an element deposited onto an electrode at a fixed potential is generally proportional to the deposition time provided the bulk concentration of the element in solution and the nature of the electrode surface is not substantially altered during deposition.

(c) *Mass transport.* Where mass transport phenomena are rate determining, the deposition current will be increased by stirring the solution and/or rotating the working electrode.

However, constancy in the rate of solution agitation or electrode rotation is essential for reproducible depositions. Mass transport also increases with temperature to the extent of ca. 2% per °C.

(d) *Electrode considerations.* The rate of deposition and the nature of the deposit varies with the type of electrode material in use and may even vary with different electrodes of the same material and manufacturer (Hamilton 1976). The overall rate of deposition is also a function of the surface area of the working electrode and stirring rate.

(e) *The supporting electrolyte.* The electrolyte used for an ASV determination is selected on the basis of solubility of reactants and products, the accessible potential range, and the effect on the electrode reaction of complexation, buffering capacity and double layer and specific absorption effects. Solubility of the reactants and products of the oxidation/reduction processes is necessary for even distribution in the solution and for the reactions to take place. The potential at which hydrogen reduction becomes a problem is largely determined by the pH of the solution, while the anions in solution usually determine the oxidation potential of the electrode material and therefore the anodic potential range of the electrode. The rate of deposition changes with electrolyte composition and concentration.

THE STRIPPING PROCESS

Electrode rotation and solution agitation is usually stopped about 20-30 seconds before the stripping step commences so that convection within the solution can slow down and so reduce the non-faradaic component of the stripping current. In normal practice, the cell circuit is not interrupted during solution quiescence, so deposition continues at a decreased rate during this period and for portion of the stripping period.

The stripping process is indirectly dependent on the experimental parameters used in the deposition process and on a number of other parameters, all of which affect stripping peak characteristics such as the stripping peak height, peak width, peak potential and peak symmetry.

Increasing the *scan rate* during the stripping step increases stripping peak heights, but at the expense of also increasing the non-faradaic current component. Peak separation also falls off as scan rate is increased. *Waveforms superimposed* on the voltage ramp (such as differential pulse) may increase the ratio of faradaic/non-faradaic current (Copeland & Skogerboe 1974), but with metal electrodes (and particularly the thin gold-film electrode), no significant improvement is attained (Forsberg *et al.* 1975), probably because of the relatively long time the charging (non-faradaic) current takes to decay after the application of the voltage pulse.

The choice of electrolyte affects resolution during the stripping step because of its influence on the potential at which oxidation peaks occur and the shape of these peaks. Electrolytes are chosen which give well defined and well separated peaks for the species being analysed. If an electrolyte interferes with the stripping process and control over the electrolyte is not possible, then solution exchange after the deposition step may be necessary (Kuwabara 1973).

Three methods of *standardising* stripping peak heights are used with ASV, *viz.* standard additions, internal standard and standard curve. Standard addition (Franke *et al.* 1978) is used extensively in ASV analyses. It requires that the analyte spikes experience the same matrix interactions as the natural species, and the relationship between stripping current and concentration must be linear. The internal standard method (Copeland *et al.* 1974a) appears, at first glance, to be a more attractive proposition than the standard addition method because it is simple and minimises analysis time. But the element chosen as the internal standard must be affected by the solution matrix in the same way and preferably to about the same extent as the analyte species, its analytical response must bear a linear relationship with concentration, it must not form inter-element compounds with the other metals present, and it should be absent originally from the sample. Standardisation with calibration curves is little used in ASV because even very small changes in the matrix composition of successive samples,

or in the condition of the working electrode surface, can have a significant effect on the electrode's response to the analyte.

INTERFERENCES IN ASV

Practically all the interferences commonly encountered in ASV can be categorised into three types:

(a) *Solution chemistry effects.* Both the electrodeposition and stripping processes in ASV can be markedly influenced by the nature of the electrolyte, electroactive impurities including surface active substances in solution (Batley & Florence 1976), and by the presence of oxygen. The extent of interference from these sources depends on the element being determined and the type of electrode used. Complexing agents interfere with analyses by retarding the deposition of species onto the electrode, although the addition of complexing agents has been used to advantage in reducing peak overlap. Sorption of surface active substances can affect both the height and potential of oxidation peaks in ASV (Brezonik *et al.* 1976).

(b) *Overlapping stripping peaks.* ASV is a relatively unselective technique. The voltage range available with the gold electrode for instance, is about 1500 mV, and if two peaks occur within less than 100 mV of each other, peak overlap may be a significant problem. Fortunately, there are a variety of ways to improve selectivity for any particular application. Selective depositing and stripping are two methods. In selective depositing, the working electrode is held at a potential at which one or more of a number of electroreducible elements is preferentially

reduced. Selective stripping involves stopping the voltage scan during an oxidation peak, allowing that element to oxidise completely, and then recording the closely spaced oxidation peak of a second element. Overlapping peaks can sometimes be separated simply by employing an electrolyte, the anion of which preferentially complexes one or more of a number of interfering elements (Gillain *et al.* 1979). Such complexation produces a negative shift in both the deposition and stripping potential which increases with both the stability of the complex formed and the concentration of that electrolyte. Multidentate ligands such as EDTA can also be used to alter the reduction and oxidation potential of an element. The selective inhibition of interfering electrode reactions by the use of surface active substances has found some application (Neeb & Kiehnast 1970).

(c) *Formation of inter-element compounds.* An interference effect common in thin-film ASV is that caused when one or more elements on the electrode surface interferes with the anodic stripping process of another by forming inter-element compounds with it (Neiman *et al.* 1980). These interactions are almost always detrimental to the analysis and should not be confused with reactions between the deposited element and the electrode material which are often beneficial and which are discussed later in this chapter. The effects of inter-element formation are to change the stripping potential of the elements involved, distort their stripping peaks, lower the sensitivity of the technique for those elements and to interfere with standardisation. The thin-film electrode is

much more prone to this type of interference than the hanging mercury drop electrode because the concentration of elements in the mercury drop is orders of magnitude lower than in the thin film.

THE GOLD ELECTRODE

The gold electrode is the working electrode of choice for applications where positive potentials up to and beyond +1 V are used. In non-complexing media at low pH values (e.g. in nitric, sulphuric and perchloric acids), the working potential range of the gold electrode is about -0.35 to +1.3 V vs. SCE. The limiting factor at the cathodic end of the potential range is hydrogen reduction, and at the anodic extreme, oxygen evolution. In halide media, the anodic extreme is limited to about +0.6 V by oxidation of the metal to complex halides.

Although +1.3 V is generally considered to be the positive limit of gold's potential range, the practical range extends little further than +1.0 V because of interference with electrode reactions, and an increasingly sloped base line, due to oxidation of the gold surface. Such oxide formation appears as an anodic wave preceding oxygen evolution on anodic scans. When working with current peaks around 1 μ A or less, this anodic wave represents the limit of operation in electroanalytical work.

In terms of the available potential range, gold is a better electrode material than platinum because it exhibits a higher hydrogen overpotential and undergoes oxidation at more positive potentials. Gold also does not absorb hydrogen films to a significant extent - a troublesome phenomenon associated with the use of platinum electrodes (Adams 1969).

The one practical disadvantage of gold as an electrode material is that it is difficult to seal in glass, and this may be at least partly responsible for its lesser popularity in the past than the platinum electrode.

All factors which affect the surface prior to, during, and even after the electrode reaction are of concern when one discusses electrode behaviour. The dropping mercury electrode has achieved its prominence due to the ease with which the electrode surface is completely renewed with each falling drop. Probably the most serious problem in solid electrode methodology is associated with understanding the true electrode behaviour and its effect on electrode processes. Separating those parts of the observable electrochemistry which belong only to the electroactive system from those determined by the electrode surface is often very difficult.

The true surface of a solid electrode is very rough in microscopic detail and consists of a maze of cracks, holes and projections. Such a surface will naturally tend to occlude various foreign materials from the solution and once incorporated into the obscure crevices and holes, these substances may be very difficult to remove. Such occlusions are often detrimental to electrode properties. Adsorption of solution components onto electrode surfaces, besides being a problem in itself, may serve as the pathway to later occlusion into the electrode matrix.

Removing contamination from the electrode surface is often very difficult, requiring strong oxidation/reduction, or high temperatures and chemical treatment in the case of organic contamination. Removal of mercury from the surface of a gold electrode by other than physical means is virtually impossible (Adams 1969).

The advantage of the *gold-film electrode* over the solid gold electrode, besides the saving in cost, is the ease with which the gold surface is renewed in the event of contamination; the gold film is simply wiped off and a new one deposited onto the electrode substrate (typically glassy carbon). The electrochemical properties of the gold-film electrode are qualitatively the same as the solid gold electrode. With both solid gold and gold-film electrodes, carefully controlled pretreatment of the electrodes is necessary to ensure reproducible electrode response. Pretreatment procedures are described later in this work. The gold electrode has a number of advantages over carbon electrodes. Deposits bond better to gold (and to metallic electrodes in general) than to carbon, particularly the semimetallic deposits considered in this work. When these elements are deposited onto a carbon surface, the deposit tends to be partly dislodged from the electrode surface by solution agitation, necessitating codeposition with metals such as copper which bond more tightly to the carbon surface. Gold has one further advantage with respect to inter-element compound formation between codeposited species. Because many of the elements that have been co-determined at the gold

antimony) interact with the gold surface, mutual interference through inter-element compound formation is minimised or eliminated altogether. Inter-element compound formation is a problem because as the concentration of one interacting element changes with respect to another (e.g. with standardisation by standard addition), its degree of interference (and so the electrode response) changes. Interaction between deposited elements and the gold surface is not subject to these fluctuations because of the excess of gold present.

A limitation of many solid electrodes is the limited success in using such waveforms as differential pulse (Forsberg 1975). In the present work with the gold-film electrode, differential pulse waveforms themselves generated more charging current through application of the voltage pulses than they were able to discriminate against and eliminate; d.c. ramps gave the lowest base line slopes and were used exclusively.

Standardisation by standard addition is mandatory when using the gold-film electrode because even when duplicate samples are analysed in sequence with conditioning of the electrode between analyses, electrode response varies as much as 10% from one analysis to the next. The reasons for these variations were not established.

Chapter 3

EXPERIMENTAL

APPARATUS

Voltage ramps were generated by a PAR-175 Universal Programmer linked to a PAR-174 potentiostat and current-to-voltage converter. Output voltage was recorded on a *Houston 2000* X-Y recorder. A PAR-173 Potentiostat/Galvanostat and PAR-179 Digital Coulometer were used for coulometric measurements. PAR cells and glassy carbon electrodes were used, in conjunction with a saturated calomel electrode (SCE) and a platinum auxiliary electrode. The SCE was isolated from the sample solution by a salt bridge containing 0.5 M sodium nitrate. Flow of moist high-purity nitrogen into the cell was directed through one of two valves: the first allowed the gas to bubble through the solution for purging while the second directed the gas over the top of the solution during an analysis. These valves were operated by an automatic controller as were all stages of the ASV analysis. Details of this controller (Hamilton *et al.* 1979) are described in Chapter 5.

REAGENTS

"ARISTAR" (B.D.H.) grade nitric acid, sulphuric acid, hydrochloric acid and ammonia solutions were used without further purification. Standard solutions of selenium, tellurium and arsenic (0.05 M) were made by dissolving the respective sodium or potassium salt (B.D.H. >99%) in water; standard solutions of antimony (0.05 M) were made by dissolving antimony trioxide (B.D.H. >99%) in aqua regia. These solutions were diluted each day to give the working solutions (1-7.5 ppm). The gold (III) stock solution was made by dissolving gold sponge (Fluka, 99.9995%) in a minimum of aqua regia and diluting with 1 M nitric acid. Sodium perchlorate was "SUPRAPUR" (Merk) grade and sodium sulphite was "ANALAR" (B.D.H.) grade. All other reagents used in this work were "ANALAR" grade. Water was distilled and redistilled twice from quartz. Chelex 100 resin (*Bio-Rad Laboratories*) was 100-200 mesh and was regenerated by washing with 2 M nitric acid ("ANALAR"), water, 0.5 M ammonia solution ("ANALAR") and finally with 0.1 M ammonia solution ("ARISTAR").

ELECTRODE PREPARATION

Before each deposition of a gold film, the electrode was polished for approximately 2 min with alumina powder (0.5 μm) and then washed successively with methanol, nitric acid and distilled water. The electrode was submerged in 15 mL of 0.1 M sodium perchlorate and left in open circuit during a 20 min purge with nitrogen. An aliquot of gold (III) solution was added (to give $[\text{Au}] = 50 \text{ ppm}$) and the solution purged for a further 5 min. After ensuring that gas bubbles were not lodged on the surface of the GCE, -0.2 V was applied to the electrode and 0.02 coulombs of gold deposited on the electrode surface (28 mm^2). For optimum performance, the electrode was kept in purged 0.1 M nitric or sulphuric acid for 24 h before use and stored under these conditions between analyses.

PROCEDURE FOR SELENIUM AND TELLURIUM DETERMINATION

A copper sample (0.5 g) was dissolved in 2 mL of 15 M nitric acid. Upon dissolution, the solution was warmed to 80-90°C to drive off most of the nitrous fumes and 0.6 mL of hydrogen peroxide (500 ppm) added. After 10 min, the solution was cooled and 3 mL of 15 M ammonia solution added. The ammoniacal solution was added to the column of Chelex 100 resin (1.5 X 12 cm), washed onto the column with a minimum of 0.1 M ammonia solution. The column was eluted with 0.1 M ammonia solution and the eluate collected in a 50 mL volumetric flask containing 2 mL of 15 M nitric acid until the flask was full to the mark.

Ten mL of the eluate was pipetted into the cell and the solution purged with nitrogen for 15 min before immersing the gold-film electrode. With the auxiliary electrode in open circuit and the working electrode earthed, the solution was purged for a further 5 min. Stirring was commenced, the working electrode conditioned for 30 s at +1.2 V, and then selenium and tellurium were deposited on the working electrode at -0.1 V for 20-200 s, depending on analyte concentration. Stirring was stopped and, after 20 s, the working electrode was scanned from -0.1 V to +1.2 V at 40 mVs⁻¹. The procedure was repeated from the conditioning step until a stripping peak of constant height was obtained for tellurium (usually 2 cycles). A Te(IV) spike was added so that the Te(IV) concentration was doubled, and the ASV determination repeated. The determination was repeated with a second spike

to verify linearity of electrode response. After verifying that a constant selenium stripping peak had been attained, one or two standard additions of Se(IV) were made to the same solution in the cell.

PROCEDURE FOR ARSENIC AND ANTIMONY DETERMINATION

A copper sample (0.5 g) was dissolved in 2 mL of 15 M nitric acid. After dissolution, the sample solution was heated briefly to expel most of the nitrous oxide fumes and diluted with an equal quantity of water. Three mL of 15 M ammonia solution was added, the solution stirred to dissolve any insoluble hydroxide and eluted through a column (1.5 X 12 cm) of Chelex 100 cation exchange resin with 0.1 M ammonia solution. Fifty mL of eluate was collected, acidified with 3 mL of concentrated sulphuric acid, and evaporated to sulphuric acid fumes to expel the bulk of the nitrate as nitric acid. The solution was cooled to 80°C and 3 mL of sodium sulphite (50% w/v) (heated to 70-80°C) added in a single addition. The solution was stirred, kept for 30 min at about 80°C, then boiled for a few min to decompose the last of the sodium sulphite. The warm solution was transferred to a 25 mL volumetric flask, allowed to cool, and diluted to volume. Analysis of this solution, as described below, was performed in two parts. Firstly, a joint determination of arsenic and antimony was made, and secondly a determination of antimony alone was made at a more anodic deposition potential in the same solution. The arsenic concentration was calculated by difference.

An aliquot of sample (5 or 10 mL) was pipetted into the cell and purged with nitrogen for 15 min before immersing the gold-film electrode. Then, with the auxiliary electrode

in open circuit and the working electrode earthed, the solution was purged for a further 5 min. Stirring was commenced, the working electrode conditioned for 30 s at +0.9 V, and then arsenic and antimony deposited on the working electrode at -0.3 V for 10-500 s, depending on their concentrations. Stirring was discontinued and, after 20 s, the working electrode voltage was scanned from -0.3 to +0.9 V at 40 mVs^{-1} and the resulting voltammogram recorded. The procedure was repeated once from the conditioning step to ensure a constant peak height. A spike of standard As(III) solution (sufficient to double the peak height) was added and the ASV determination repeated. At a deposition potential of -0.3 V, the electrode response to As(III) and Sb(III) was the same, thus making it unnecessary to add to standard addition of Sb(III).

To determine the concentration of Sb(III) in the solution, the deposition potential was adjusted to -0.05 V and the procedure used for the As-Sb determination was repeated, but with addition of Sb(III) in place of As(III). Arsenic was not deposited on the electrode at this potential.

Once the concentration of Sb(III) had been calculated, the concentration of As(III) could be obtained by using the following formula:

$$[As] = \frac{C_{As} \times P_1}{P_2} - [Sb]$$

where

- C_{As} = increase in As(III) concentration in the sample due to the standard As(III) addition
- P_1 = the height of the initial As-Sb peak
- P_2 = increase in peak height due to standard As(III) addition.

COMBINED ANALYSIS PROCEDURE

A copper sample (0.5 g) was dissolved in 2 mL of 15 M nitric acid. Upon dissolution, the solution was heated to 80-90°C to expel most of the nitrous fumes and 0.6 mL of hydrogen peroxide (500 ppm) was added. After 10 min, the solution was cooled and 3 mL of 15 M ammonia solution added. The sample was stirred to dissolve any undissolved hydroxide, and eluted through a column of Chelex 100 ion exchange resin (1.5 X 12 cm) with 0.1 M ammonia solution. Fifty mL of eluate was collected and acidified with 3 mL of concentrated sulphuric acid. The 50 mL of solution was split into two equal portions. One 25 mL portion was analysed directly for selenium and tellurium, the other required further work-up before analysis for arsenic and antimony.

SELENIUM AND TELLURIUM DETERMINATION

Five mL of the eluate was pipetted into the cell and the solution purged with nitrogen for 15 min before immersing the gold-film electrode. With the auxiliary electrode in open circuit and the working electrode earthed, the solution was purged for a further 5 min. Stirring was commenced, the working electrode conditioned for 30 s at +1.2 V, and then selenium and tellurium were deposited on the working electrode at -0.1 V for 20-200 s, depending on analyte concentration. Stirring was stopped and, after 20 s, the working electrode was scanned from -0.1 V to +1.2 V at 40 mVs⁻¹. The procedure was repeated from the conditioning step until a

stripping peak of constant height was obtained for tellurium (usually 2 cycles). A Te(IV) spike was added so that the Te(IV) concentration was doubled and the ASV determination repeated. The determination was repeated with a second spike to verify linearity of electrode response. After verifying that a constant selenium stripping peak had been attained, one or two standard additions of Se(IV) were made to the same solution in the cell.

ARSENIC AND ANTIMONY DETERMINATION

The second 25 mL portion was evaporated to sulphuric acid fumes to expel the bulk of the nitrate as nitric acid. The solution was cooled to 80°C and 1.5 mL of sodium sulphite (50% w/v) (heated to 70-80°C) added in a single addition. The solution was stirred, kept for 30 min at about 80°C, then boiled for a few min to decompose the last of the sodium sulphite. The warm solution was transferred to a 10 mL volumetric flask, allowed to cool, and diluted to volume. Analysis of this solution, as described below, was performed in two parts. Firstly, a joint determination of arsenic and antimony was made, and secondly a determination of antimony alone was made at a more anodic deposition potential in the same solution. The arsenic concentration was calculated by difference.

An aliquot of sample (5 mL) was pipetted into the cell and purged with nitrogen for 15 min before immersing the gold-film electrode. Then, with the auxiliary electrode in

open circuit and the working electrode earthed, the solution was purged for a further 5 min. Stirring was commenced, the working electrode conditioned for 30 s at +0.9 V, and then arsenic and antimony deposited on the working electrode at -0.3 V for 10-500 s, depending on their concentrations. Stirring was discontinued and after 20 s, the working electrode voltage was scanned from -0.3 to +0.9 V at 40 mVs^{-1} and the resulting voltammogram recorded. The procedure was repeated once from the conditioning step to ensure a constant peak height. A spike of standard As(III) solution (sufficient to double the peak height) was added and the ASV determination repeated. At a deposition potential of -0.3 V, the electrode response to As(III) and Sb(III) was the same, thus making it unnecessary to add a standard addition of Sb(III).

To determine the concentration of Sb(III) in the solution, the deposition potential was adjusted to -0.05 V and the procedure used for the As-Sb determination was repeated, but with addition of Sb(III) in place of As(III). Arsenic was not deposited on the electrode at this potential.

Once the concentration of Sb(III) had been calculated, the concentration of As(III) could be obtained by using the formula described in the previous analytical procedure.

Chapter 4

RESULTS & DISCUSSION

INTRODUCTION

Selenium and tellurium belong to group VI of the periodic table and, in most respects, they display the metalloid properties of this group. The presence of six electrons in the outer shell determines the valency states of -2 and +6, although in their most stable forms, selenium and tellurium are tetravalent. Selenium(IV) exists in solution as the selenite (SeO_3^{2-}) ion, and Selenium(VI) as the selenate (SeO_4^{2-}) ion. Selenites are reduced to the element by sulphurous acid and to the selenide by an aqueous solution of hydrazine (Rosenfeld & Beath 1964). . Oxidation to the VI state requires strong oxidising agents such as permanganate or hydrogen peroxide. Elemental selenium is oxidised to the selenite ion by the action of nitric acid.

Tellurium(IV) exists in solution as tellurite (TeO_3^{2-}), and tellurium(VI) as tellurate (TeO_4^{2-}). The oxidation/reduction properties of tellurium closely resemble those of selenium (Green & Turley 1961).

Arsenic and antimony are in the fifth group of the periodic table along with nitrogen, phosphorous and bismuth. Their principal oxidation states are +5, +3 and -3. The As^{3+} cation exists only in strongly acid solutions; under less acid conditions, the tendency is towards hydrolysis, so that the anionic form, the arsenite ion, (AsO_3^{3-}), predominates (Skonieczny 1978).

Antimony does not exist as a simple cation in aqueous solution, but as partially hydrolysed species such as Sb(OH)^{2+} in the case of Sb(III) ions, and Sb(OH)_2^{3+} with Sb(V) ions. In strong hydrochloric acid solution, Sb(III) exists as chloroantimonous acid (HSbCl_4), and when diluted with water it rapidly hydrolyses to a series of insoluble compounds (Hahn 1978). However in considering nitric or sulphuric acid solutions, where the concentration of Sb(III) is in the low ppb range, Sb(III) appears to remain in the form of soluble electroactive species. Keeping antimony in solution under these conditions does not seem to be the problem one might expect.

Selenium and tellurium in their highest valence state (+6) are electrochemically inactive in most electrolytes. Similarly, arsenic and antimony are electrochemically inactive when in the +5 state. However, arsenic and antimony can be electrochemically reduced from the +3 to the elemental state and through to the -3 state. They may also be oxidised stepwise to the +5 state. Selenium and tellurium may be reduced and oxidised stepwise between the +4, elemental and -2 states. Oxidation to the +6 state is beyond the scope of most electrodes due to oxygen evolution.

INVESTIGATION OF ANALYTICAL METHODS

The initial exploratory work was done with selenium, as this element has received more attention in the literature than the other three. The method of determining Se(IV) by its *codeposition with copper* on a glassy carbon electrode (GCE) and subsequent ASV analysis in 0.1 M hydrochloric acid was investigated. Se(IV) and Cu(II) were reduced to the corresponding element during the deposition and then oxidised back to the original oxidation states during the stripping step. The copper served to bind the selenium deposit to the electrode. Krapivkina *et al.* (1975) reported that during the anodic scan (after a timed deposition at -0.6 V), three peaks were obtained; a copper oxidation peak at -0.05 V, a peak corresponding to the oxidation of the Cu-Se inter-element compound at +0.2 V and a selenium oxidation peak at +1.05 V. The peak corresponding to oxidation of the inter-element compound was found to be the most sensitive peak for selenium.

Krapivkina's procedure was followed, and although no selenium oxidation peak was found around -1.0 V, there was a peak at +0.22 V. The copper peak occurred as a large multiple peak with maxima at -0.06 V and +0.12 V. The occurrence of the latter peak made it very difficult to establish a base line for the peak at +0.22 V. Such multiple peaks for copper have been reported previously (Vassos 1965; Vassos & Mark 1967). The peak at +0.22 V increased with Se(IV) concentration, although the calibration graph was

markedly curved. Also, the electrode response was found to deteriorate significantly from one deposition-scan cycle to the next and so the surface of the glassy carbon electrode required frequent repolishing to restore its performance. By using a deposition potential of -0.4 V, the calibration curve was improved, but the method remained quite unacceptable.

CSV using the hanging mercury drop electrode was also investigated. The method was first proposed by Vajda (1970) and involves reduction of Se(IV) to the element on the mercury electrode at a potential of -0.4 V and subsequent stripping of the deposit as the hydride at -0.55 V. To obtain reproducible stripping peaks from one deposition-scan cycle to the next, it was necessary to extrude a new mercury drop before each deposition. This would preclude future automated analysis. Concentrations of copper and tellurium equal to that of the selenium significantly interfered with the analysis of selenium.

A thin mercury-film electrode was used in place of the hanging mercury drop electrode, but no selenium reduction peaks were found at all. Both pre-formed and *in-situ* films were tested, but without success.

The method finally chosen for the analysis of Se(IV) was ASV at a gold-film electrode. This method gave excellent sensitivity and offered the potential of finding a procedure for the joint determination of all four elements (selenium, tellurium, arsenic and antimony). Andrews & Johnson (1975,

1976) analysed down to 0.04 ppb Se(IV) in pure electrolyte solutions using a rotating gold-disk electrode (55 mm^2) and Forsberg *et al.* (1975) determined As(III) in concentrations down to 0.02 ppb in pure hydrochloric and perchloric acid solutions with a gold electrode (8 mm^2). Davis *et al.* (1978) successfully analysed As(III) concentrations down to about 5 ppb in hydrochloric acid solution with a gold-film (gold on graphite) electrode. No references to the determination of tellurium or antimony using gold or gold-film electrodes were found.

CYCLIC VOLTAMMETRY AT THE GOLD-FILM ELECTRODE

The electrochemical behaviour of selenium, tellurium, arsenic and antimony in solution at the gold-film electrode was studied using cyclic voltammetry. Directly before the study, the GCE was plated with 0.02 coulombs of gold in the manner described in Chapter 3. The condition and surface area of the gold film were checked periodically and found not to change significantly during the study. The condition of the gold film was measured by its analyte response to selenium, and the surface area was monitored by measuring the area of the gold oxide reduction peak at +0.82 V. The limits of potential scan were -0.4 V and +1.3 V and all potentials were measured against the SCE. The scan rate was 40 mVs⁻¹ and the base electrolyte was 0.1 M sulphuric acid. All voltammograms were run in stirred solutions.

Figure 1 shows the residual voltammogram obtained with the thin gold-film electrode in the base electrolyte. The limiting cathodic process is hydrogen evolution which occurs cathodic of -0.4 V, and the limiting processes at the anodic extreme are oxidation of the surface of the gold film and oxygen evolution. These processes occur anodic of +1.0 V. Oxidation of the gold surface occurs to a varying extent, dependent on the potential to which the electrode is subjected (Ferro 1974). At +1.3 V, oxidation is limited to the few atomic layers closest to the surface of the electrode. The oxidation product is reduced during the cathodic scan, giving the peak at +0.82 V. The small waves observed on the

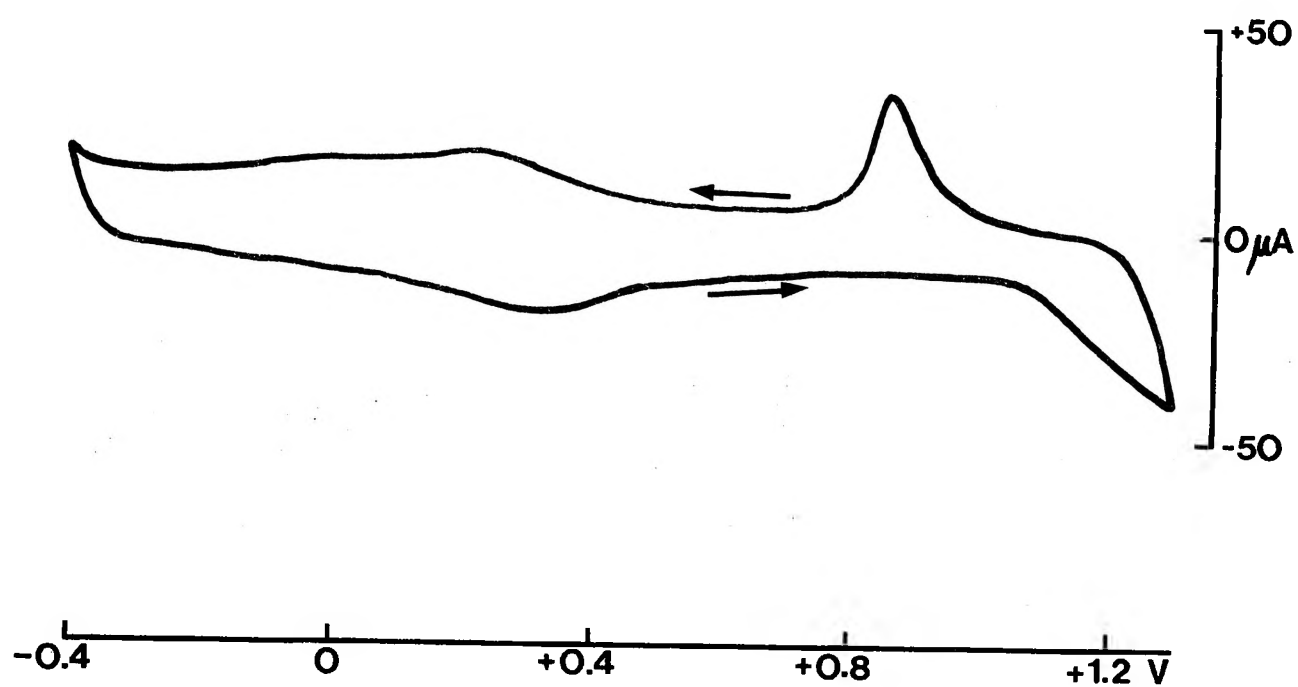


FIGURE 1 Residual cyclic voltammogram at the gold-film electrode. Electrolyte 0.1 M H_2SO_4 , scan rate 40 mVs^{-1} .

cathodic scan around +0.2 V, and on the anodic scan at +0.35 V, appear to be typical of the glassy carbon/gold-film electrode. They can be found in other published voltammograms where the same type of electrode has been used (Andrews & Johnson 1975). The GCE and solid gold electrodes do not give these waves.

The residual voltammogram has been superimposed as a dashed line on the succeeding voltammograms. In each of the four figures, *curve (a)* was recorded for an analyte concentration of 0.3 ppm and *curve (b)* for a concentration of 3 ppm. The peak potentials derived from the cyclic voltammetry studies may not match exactly those quoted for the same reaction in the ASV work because peak potentials at metal-film electrodes are dependent on many factors including deposition time, analyte concentration and the condition of the electrode surface.

SELENIUM

Curve (a) of Figure 2 shows a single peak which corresponds to the oxidation of Se(0) to Se(IV). The cathodic scan portion of curve (b) shows two selenium reduction peaks, at +0.12 and -0.13 V. Peak A is reported to be due to reduction to As(0) of As(III) previously adsorbed onto the electrode surface during the earlier portion of the scan; the general increase in current around peak B corresponds to the convective-diffusion deposition of Se(IV) from solution (Andrews & Johnson 1975).

The multiple oxidation peaks obtained for selenium, and shown in curve (b), are indicative of multiple states of activity within the deposit, resulting from various degrees of interaction with the gold surface. The stripping of small deposits of selenium gives one peak (curve (a)) at +0.83 V, and corresponds to oxidation of up to one monolayer of selenium which is strongly adsorbed onto the surface of the electrode. Oxidation of a complete monolayer corresponds to the limiting peak height of 45 μ A (curve (b) - peak D). Deposition of selenium beyond the monolayer gives rise to two more oxidation peaks in the subsequent anodic scan. Peak C (+0.6 V) is probably due to oxidation of bulk selenium from the electrode i.e. selenium which has been deposited on a selenium rather than a gold surface. Such a deposit is less strongly bonded and so more easily oxidised than the adsorbed selenium monolayer. Peak E (+1.0 V) is thought to correspond to oxidation of selenium which has

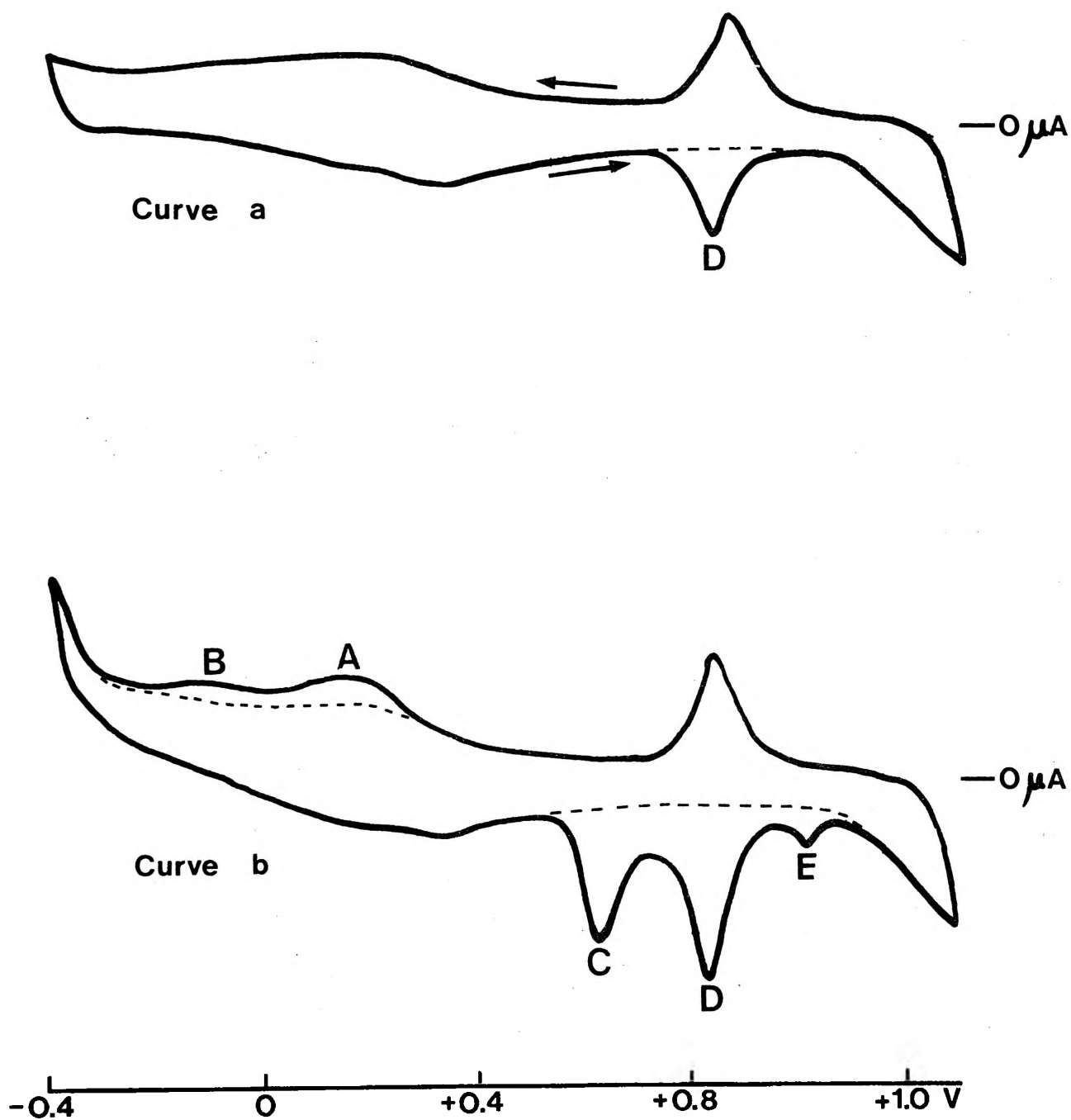


FIGURE 2 Cyclic voltammograms for 0.3 ppm (curve (a)) and 3.0 ppm (curve (b)) Se(IV) at a gold-film electrode. Electrolyte 0.1 M H₂SO₄, scan rate 40 mVs⁻¹.

formed a gold-selenium inter-element compound and diffused into the electrode (Andrews & Johnson 1975). The height of peaks C and E appear to increase without bound as Se(IV) concentration is increased.

Under normal analytical conditions, with a deposition potential of -0.1 V, only a portion of the adsorbed monolayer is deposited and only one oxidation peak (peak D) is obtained. A more detailed examination of this selenium oxidation peak is presented later in this chapter.

TELLURIUM

Deposition of $\text{Te}(0)$ and stripping as $\text{Te}(\text{IV})$ from a solution of 0.3 ppm $\text{Te}(\text{IV})$ produced only a single oxidation peak at +0.55 V as shown in *curve (a)* of Figure 3. This peak (which corresponds to peak B in *curve (b)*) is generated by oxidation of up to one monolayer of $\text{Te}(0)$ adsorbed onto the electrode surface. The limiting height of this peak was 45 μA . Deposition of further tellurium gives rise to two closely spaced oxidation peaks around +0.4 V. The height of this pair of peaks increased indefinitely with arsenic concentration, and they are presumably due to oxidation of bulk tellurium from the electrode. A peak corresponding to the third oxidation peak for selenium (peak E of Figure 2) was not found, suggesting that tellurium is less inclined to form an inter-element compound with gold. Also missing were the reduction peaks noticed in the selenium voltammograms, indicating that $\text{Te}(\text{IV})$ is not adsorbed onto the electrode at potentials anodic of those which bring about reduction to the element. A rise in the cathodic portion of the voltammogram negative of 0 V corresponds to the convective-diffusion reduction of the $\text{Te}(\text{IV})$.

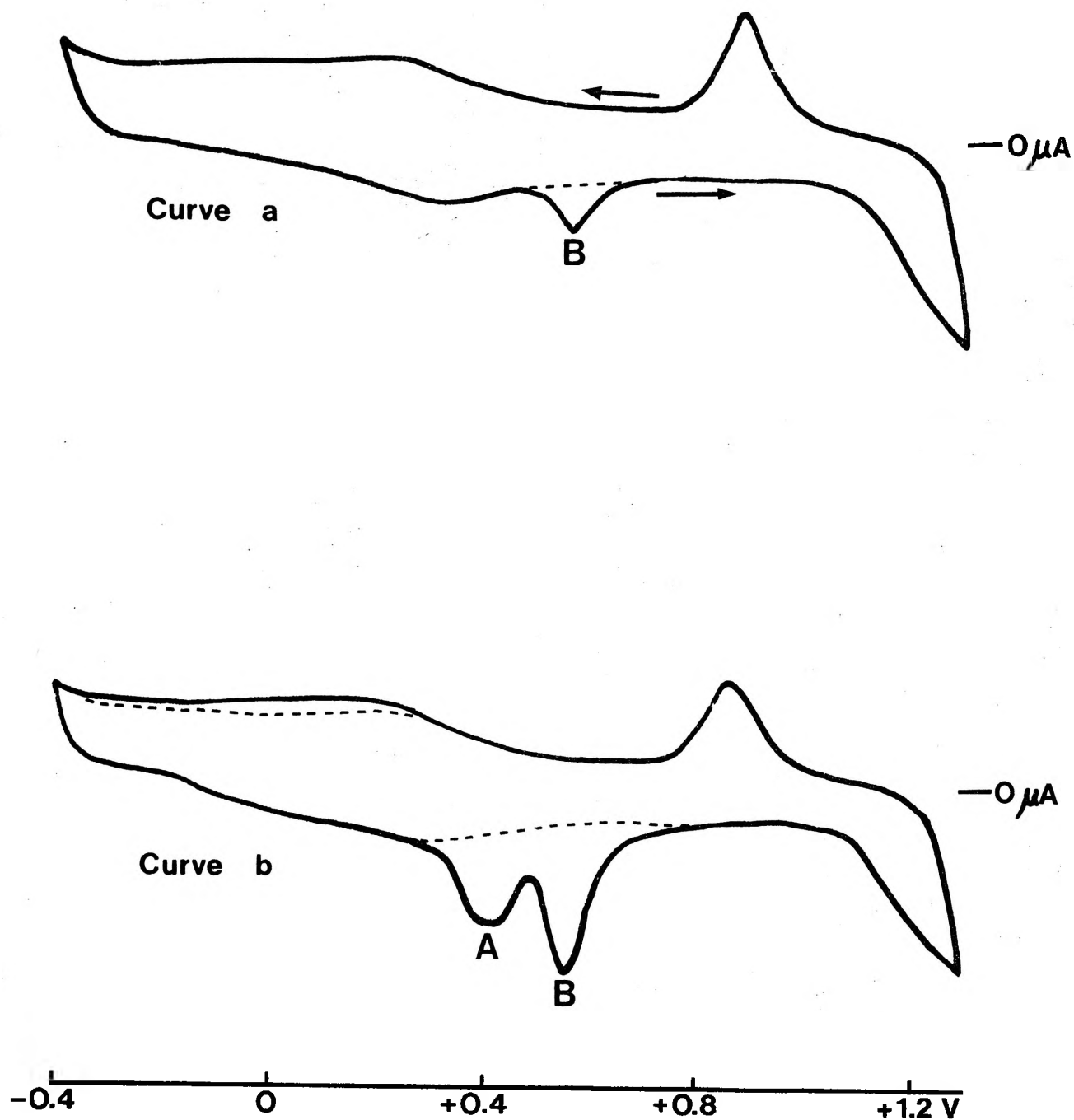


FIGURE 3 Cyclic voltammograms for 0.3 ppm (curve (a)) and 3.0 ppm (curve (b)) Te(IV) at a gold-film electrode. Electrolyte 0.1 M H₂SO₄, scan rate 40 mVs⁻¹.

ARSENIC

The peak corresponding to the reduction of As(III) to As(0) is labelled peak A in curve (b) of Figure 4, and can also be discerned in curve (a). The presence of this peak indicates As(III) adsorption onto the electrode prior to its reduction. Two peaks were obtained for the oxidation of As(0) to As(III); peak B (+0.03 V) is due to oxidation of bulk arsenic, and peak C (+0.11 V) to the oxidation of adsorbed arsenic. Peak C increased in height with As(III) concentration until it reached a limiting height of about 25 μ A. Peak B increased with As(III) concentration without bound. The behaviour of peak B appears to contradict the findings of Davis *et al.* (1978) who found that arsenic was not deposited onto an arsenic surface and attributed the finding to the nonconducting nature of elemental arsenic.

Another contradiction between our results and the literature lies in the matter of adsorption of As(III) on gold. Loucka (1973) reported that arsenious acid is adsorbed onto the electrode after oxidation from the elemental state and desorbs only after further oxidation to arsenic acid. The potential of peak D (+0.95 V) corresponds closely to the potential reported by Loucka for the oxidation of As(III) to As(V), however the peak area obtained in our work indicated that most of the As(III) formed by oxidation of the elemental arsenic had been desorbed before it could be oxidised further. This apparent contradiction may be accounted for in the much faster scan rates (2 Vs^{-1}) used by Loucka, and therefore in

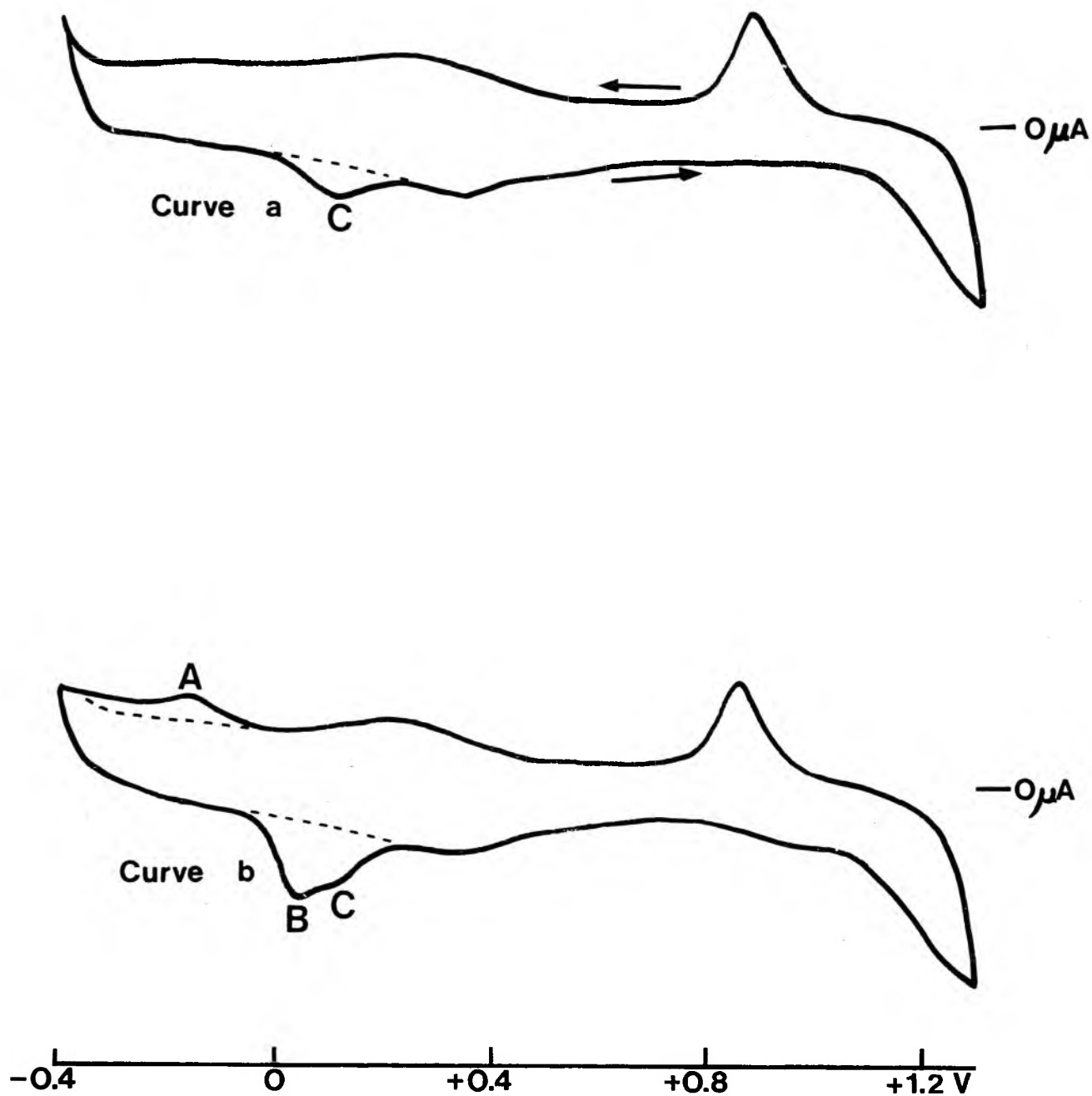


FIGURE 4 Cyclic voltammograms for 0.3 ppm (curve (a)) and 3.0 ppm (curve (b)) As(III) at a gold-film electrode. Electrolyte 0.1 M H_2SO_4 , scan rate 40 mVs^{-1} .

the different times available for desorption in each of the two experiments.

ANTIMONY

Peak A in *curve (b)* of Figure 5 occurs at -0.05 V and is due to the reduction of adsorbed Sb(III) to Sb(0). Oxidation of the elemental deposit results in a maximum of four peaks (B, C, D & E). Peak E ($+0.1$ V) is due to oxidation of the adsorbed monolayer and attains a limiting height of $25\text{ }\mu\text{A}$. As the concentration of Sb(III) was increased beyond 3 ppm, peak B (-0.15 V) increased continuously while the height of peaks C (-0.05 V) and D ($+0.05$ V) remained unchanged.

Peak F (*curve (b)*) appears to be caused by an oxidation process involving Sb(III), although the relative size of this peak indicates that oxidation of As(III) to As(V) is not the only process involved. *Curve (c)* shows a voltammogram recorded under the same conditions as *curve (b)* except that the solution was not stirred. The processes responsible for peak F and for the extra peaks in *curve (c)* were not investigated in this work.

In the ASV methods described in this work for each of the four elements, only the stripping peak corresponding to oxidation of the adsorbed monolayer was used.

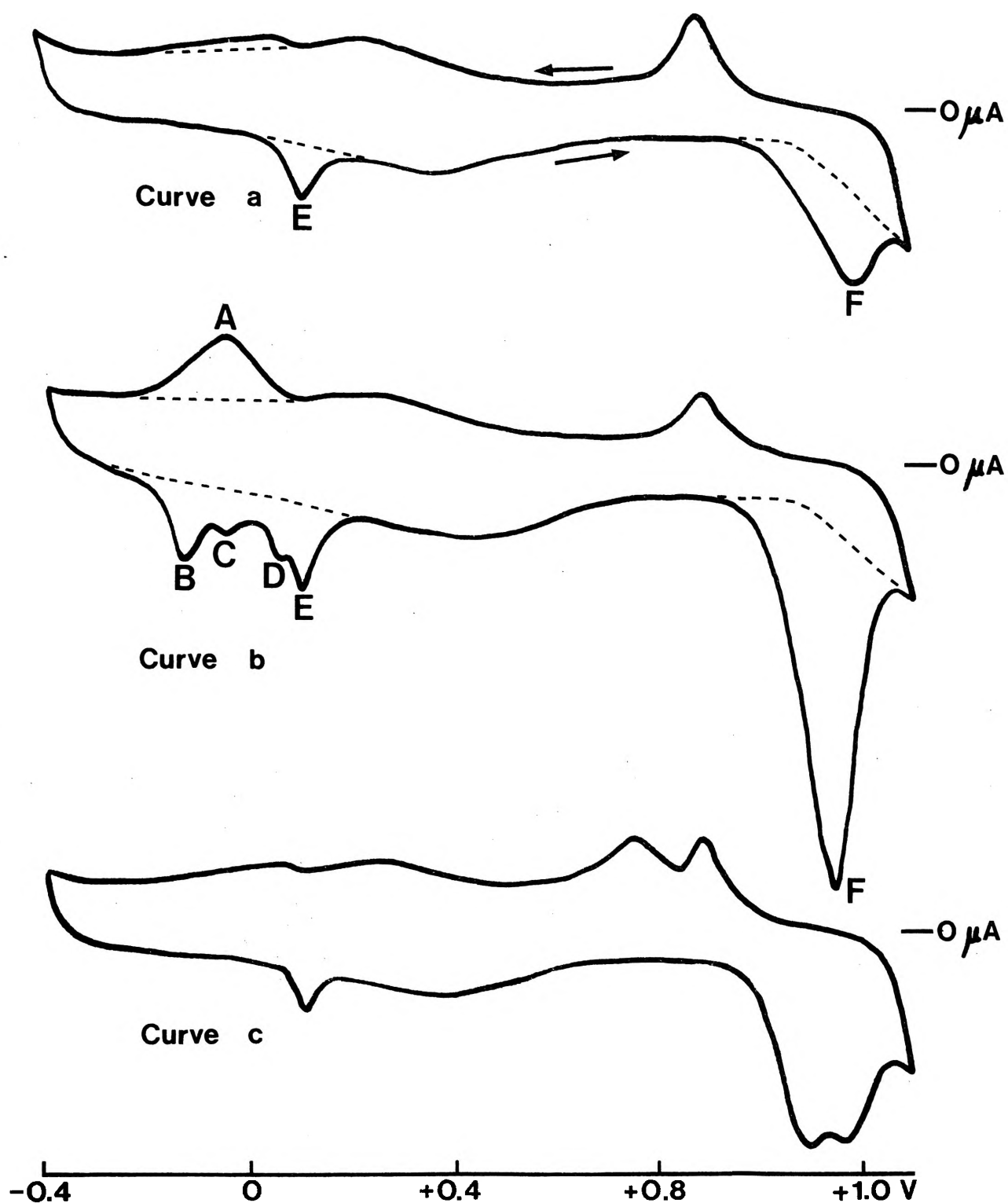


FIGURE 5 Cyclic voltammograms for 0.3 ppm (curve (a)) and 3.0 ppm (curves (b) & (c)) Sb(III) at a gold-film electrode. Electrolyte 0.1 M H_2SO_4 , scan rate 40 mVs^{-1} .

ELECTRODE CHARACTERISATION

In characterising the gold-film electrode, Se(IV) was used as the test ion. In the preparation of the gold-film electrode (described in the previous chapter), two factors which directly influence its performance in selenium analysis are: (1) the condition of the glassy carbon surface before gold deposition, and (2) the amount of gold plated on the electrode (referred to as 'film thickness').

The nature of the gold film may be compared with a mercury film. When mercury is plated onto the GCE, it is not plated on as a continuous film, but is deposited onto numerous 'active sites' on the electrode surface (Stulikova 1973) so that many small mercury droplets are formed. Continued deposition increases the size of those droplets rather than causing new ones to form. The present work indicates that gold is deposited onto the GCE in a similar manner. For example, when the rate of deposition of gold onto the GCE (measured with the aid of a digital coulometer) is plotted against time, a virtual straight line graph is obtained in depositing from 1×10^{-5} to 1×10^{-1} coulombs of gold. If gold was deposited as a continuous film, then a change in the deposition rate would be expected after the first atomic monolayer (2×10^{-4} coulombs) of gold were deposited, because gold would then begin depositing onto gold rather than onto a glassy carbon surface. The constancy in the rate of deposition of gold after 1×10^{-5} coulombs had been deposited suggests that the initial deposit

of gold on the glassy carbon electrode covered less than 4% of the electrode surface. Additional evidence to support the concept of a discontinuous film is presented further on in this section.

When a GCE is subjected to positive potentials of +0.5 V or more, its surface undergoes oxidation which gradually makes the electrode electrochemically passive. This oxidation leads to a reduction in the number of sites available for metal deposition and so reduces the effective surface area of the metal film subsequently deposited onto the electrode. Because the selenium is deposited as not more than a monolayer on the gold film at the deposition potential employed (-0.1 V), a decrease in the available surface area of the gold film causes a corresponding decrease in the deposition capacity for selenium. Thorough repolishing with diamond or alumina powder is necessary to restore the electrode's sensitivity and deposition capacity.

To demonstrate how the sensitivity of a gold-film electrode is lowered when the gold film is plated onto an oxidised glassy carbon surface, a GCE was polished thoroughly and plated with 2×10^{-3} coulombs of gold. After running several scans between -0.1 and +1.4 V to evaluate its performance, the gold film was removed from the electrode by wiping it with a tissue. Without polishing the electrode, 2×10^{-3} coulombs of gold was again plated onto the now slightly oxidised electrode and its performance measured. This procedure was repeated three more times. Figure 6

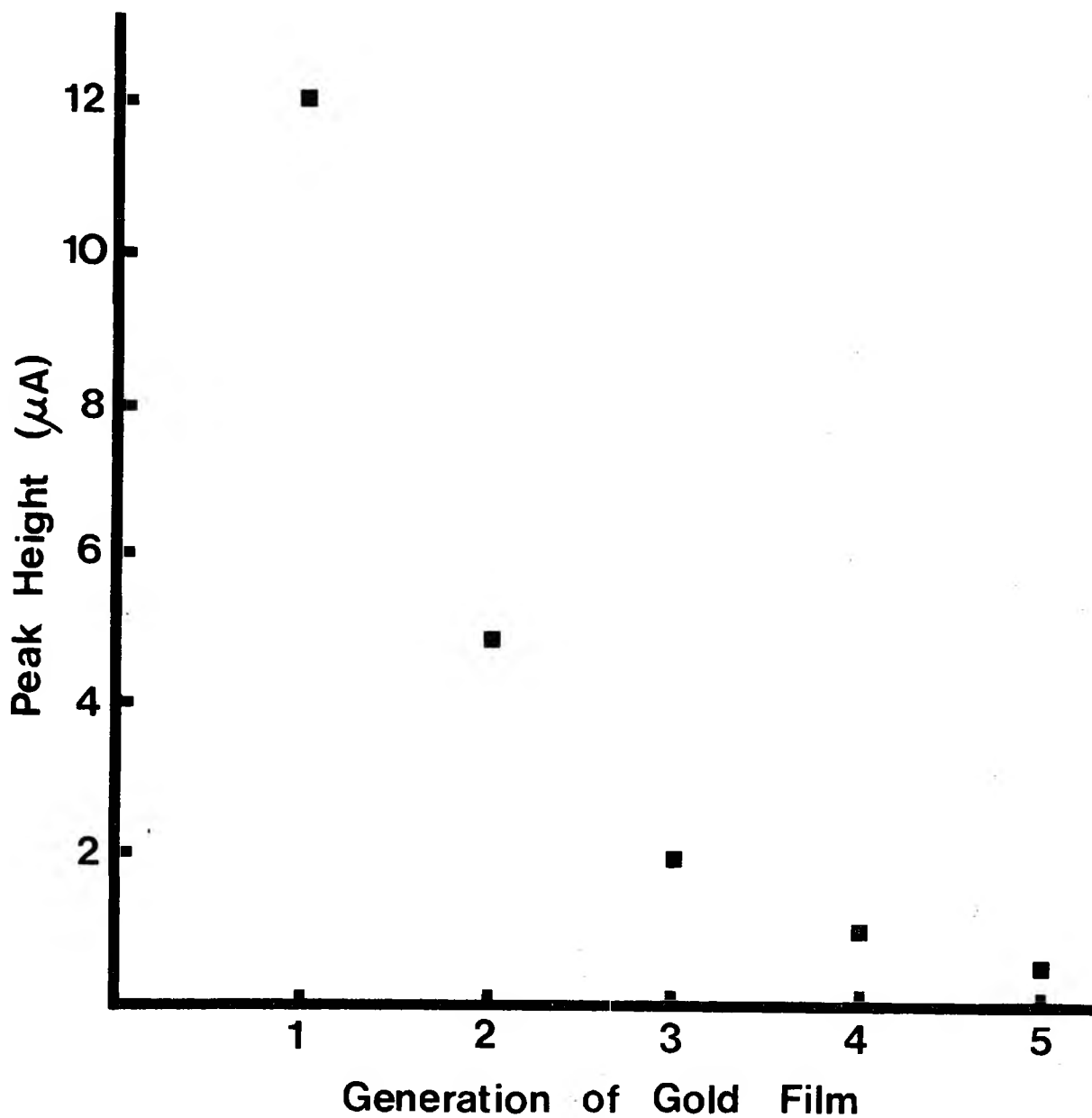


FIGURE 6 Passivation of the GCE measured as a decrease in the electrode response to selenium as successive gold films (2×10^{-3} coulombs) are plated onto the GCE.

demonstrates how the electrode's sensitivity to selenium dropped off as consecutive gold films were plated onto a progressively more oxidised glassy carbon surface. The gold reduction peak at +0.82 V, obtained by partially oxidising the electrode by subjecting it to a potential of +1.2 V and then scanning cathodically to produce the reduction peak, showed the same trend as the selenium peak in Figure 6. Loss of gold from the electrode during this oxidation/reduction treatment was negligible.

The relationship between the amount of gold plated onto the electrode (film thickness) and the selenium peak height for a 100 s deposition from a 50 ppb Se(IV) solution is shown in Figure 7. The inconsistency in the data shown in this graph was due to difficulty in obtaining a reproducible surface on the GCE prior to each gold-plating step. Nevertheless, an obvious trend is seen in the graph. A similar relationship was observed between the film thickness and the deposition capacity of the electrode. The deposition capacity is simply the amount of selenium which can be deposited on to the electrode (*i.e.* one monolayer). These findings also support the concept that gold is plated onto the glassy carbon electrode in the form of distinct deposits at active sites on the electrode, with the surface area of these deposits increasing as more gold is deposited on the electrode, rather than as a continuous film which would give rise to a selenium peak height of maximum height after the gold film thickness exceeded one monolayer (2×10^{-4} coulombs).

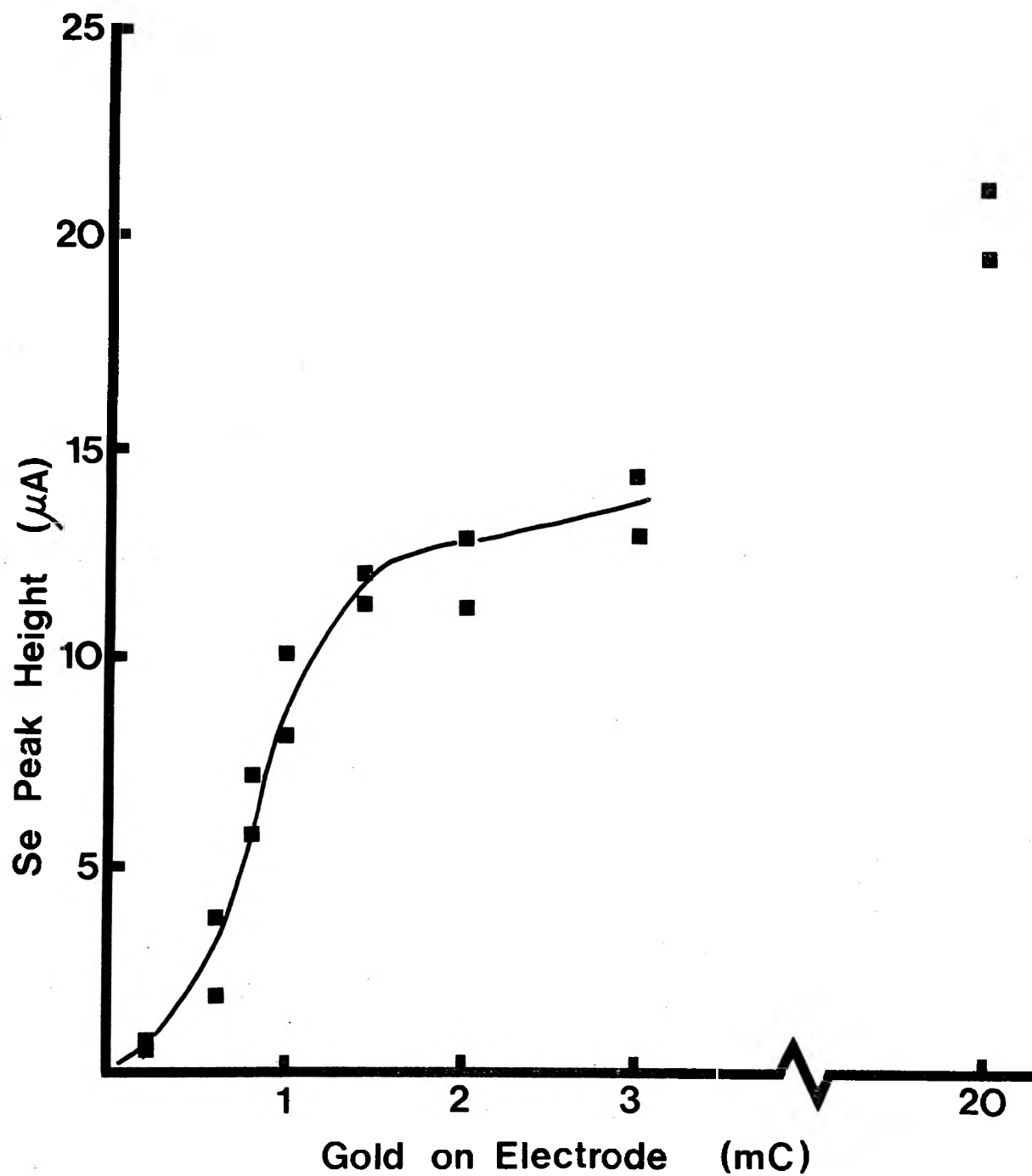


FIGURE 7 Variation of selenium peak height with amount of gold deposited; Se(IV) concentration 50 ppb, deposition time 100 s.

The gold reduction peak at +0.82 V showed the same dependence on gold film thickness as the selenium peak. Because only part of the gold film was oxidised during the oxidation period prior to the cathodic scan (the few monolayers closest to the film surface (Chen & Sard 1971)), the increase in the gold reduction peak with film thickness again suggests that the surface area of the gold film increases with film thickness.

INVESTIGATION OF SEPARATION METHODS

In solutions where the concentration of Cu(II) exceeds a few ppm, copper is codeposited with selenium at the gold-film electrode in sufficient quantities to seriously interfere with the selenium oxidation peak. If the ASV technique is to be used, the copper must be either separated from the Se(IV) in solution or prevented from depositing on the electrode by using masking agents specific for copper.

Several methods of separating small amounts of Se(IV) from an excess of Cu(II) have been discussed (Chapter 1). All of the proposed methods have serious drawbacks when applied to the problem in hand, *i.e.* separation of as little as 1 ppb of Se(IV) from as much as a 10 million times excess of Cu(II), with subsequent analysis by ASV. Solvent extraction was judged unsuitable because quantitative separation of copper is a very lengthy procedure and because traces of organic solvents left in solution interfere with ASV analysis. Separation by distillation invariably involves addition of halides and these oxidise the gold electrode at positive potentials.

Electrolytic separation of copper at controlled potential (1 A maximum current) from a solution of Cu(II) and Se(IV) was investigated, but deposition was very slow and selenium was deposited with copper at the cathode. Various masking agents were added to prevent the deposition

of selenium, but all were unsuccessful. Because most masking agents recommended for Se(IV) also complex Cu(II) to some extent, their use in the potentiometric separation invariably resulted in failure to electrodeposit the last few ppm of Cu(II). (The concentration of residual Cu(II) was proportional to the amount of masking agent added). When more cathodic potentials were used, selenium was again deposited along with the copper.

The next approach to the separation problem involved the use of *potassium ferrocyanide* to precipitate most of the copper from solution. Ferrocyanide was chosen because of the extreme insolubility of its compound with Cu(II), particularly in solutions containing ammonium salts; 0.4 ppm of Cu(II) can be precipitated with ferrocyanide in the presence of ammonium salts (Sneed *et al.* 1954). When added in 15% excess to a solution of 0.15 M copper nitrate/0.1 M ammonium nitrate containing 500 ppm of Se(IV) at pH 3, ferrocyanide precipitated all but a fraction of a ppm of Cu(II). Excess ferrocyanide was adsorbed onto the precipitate leaving less than 1 ppm of ferrocyanide in solution. The mixture was centrifuged, the clear supernatant acidified to pH 1 and then analysed for selenium. The analysis showed no Se(IV) present and standard additions of Se(IV) also failed to give a peak, until the concentration of added selenium exceeded a few hundred ppb. Above this level, the electrode's response to selenium was approximately normal. The scans obtained from the supernatant exhibited two extra peaks at +0.2 and +0.7 V.

The data from these experiments suggest that ferrocyanide complexes with Se(IV) and prevents its deposition. When the selenium concentration exceeds the capacity of the ferrocyanide to react quantitatively with it, then any excess of selenium deposits onto the electrode and gives rise to a peak during the analysis scan. The height of this peak is then seen to increase with Se(IV) concentration at the same rate as in the pure electrolyte. If the interference was due to reactions at the electrode surface, then an increase in Se(IV) concentration would not cause a significant rise in analyte response.

Successive aliquots of ferrocyanide were added to a sample of electrolyte containing 500 ppb of Se(IV) and its effect on selenium analysis was studied. Ferrocyanide, even at concentrations of less than 1 ppm, was found to reduce the selenium peak. The two peaks seen previously at +0.2 and +0.7 V were absent, even at ferrocyanide concentrations as high as 100 ppm. however, addition of a trace of Cu(II) to this sample caused the two peaks to appear.

To prevent the possible adsorption of Se(IV) onto the copper ferrocyanide precipitate, sulphate (as ammonium sulphate) was added to the solution in the hope that it would be preferentially adsorbed. The sulphate, however, prevented all but a little of the excess ferrocyanide from adsorbing onto the precipitate, and so a second cation was required to mop up residual ferrocyanide from solution. Because Zn(II) and Cd(II) do not interfere with selenium determination and

form very insoluble compounds with ferrocyanide, aliquots of each of these metal ions were added to the supernatant after the first centrifuge. The resulting precipitate was again centrifuged and the supernatant analysed after adjusting the pH to 1. Addition of Zn(II) was found to lower the ferrocyanide concentration to less than 1 ppm. Analysis of the supernatant gave virtually no Se(IV) peak, but did give the two peaks at +0.2 and +0.7 V. These two peaks were obtained at both the gold-film and glassy carbon electrodes and were present also when an excess of Zn(II) was added to a stock ferrocyanide solution and the supernatant analysed after centrifugation.

Filtering the supernatant through a 0.2 μm filter before acidification and analysis did not eliminate these two peaks in subsequent analysis. The peak heights were independent of selenium concentration and varied only a little with deposition time. They appeared only when ferrocyanide was present in solution together with Cu(II) or Zn(II). Substitution of Cd(II) for Zn(II) also failed to eliminate the interference of ferrocyanide with selenium determination. The addition of Cd(II) did not give rise to any spurious peaks. Copper removal with ferrocyanide was also attempted at pH 5, but analysis results were similar to those obtained at pH 3. At pH 2, several ppm of Cu(II) remained in solution after the precipitation.

Potassium ferricyanide was then tried in place of ferrocyanide as a precipitating agent for copper. A 5%

excess of ferricyanide was found to lower the Cu(II) concentration to below 1 ppm, but the reagent excess reduced or eliminated the selenium peak in the same manner as with ferrocyanide. Small amounts of ferricyanide alone in solution with Se(IV) reduced the peak height of the latter, but did not cause extra peaks to form. However, when ferricyanide was present in solution with Zn(II) or Cu(II), a cluster of three peaks appeared between +0.75 and +1.0 V. These three peaks were independent of Se(IV) concentration, and appeared when either a gold-film or glassy carbon electrode was used.

These spurious peaks found with both ferrocyanide and ferricyanide in the presence of either Cu(II) or Zn(II) appear to be due either to oxidation of a soluble compound or ion-association complex formed between ferrocyanide/ferricyanide and Zn/Cu(II), or to the electrochemical oxidation of ferrocyanide/ferricyanide being catalysed by these metal ions. The occurrence of these peaks at both the glassy carbon and gold-film electrode rules out gold as playing a part in the reaction.

UV irradiation of the supernatant solutions was used in an attempt to destroy any ferrocyanide or ferricyanide complexes in the solution. In subsequent voltammograms, the usual peaks were absent, but in their place was a pronounced peak, the potential of which matched that obtained from solutions containing the cyanide ion. The apparent presence of cyanide not only eliminated the selenium

peak but rendered the electrode permanently insensitive to selenium and necessitated the deposition of a new gold film.

Precipitation of copper using *sodium phosphate* was attempted, because it was found that selenium analysis was barely affected by the presence of 0.3 M phosphoric acid. When 1 M phosphate buffer of pH 6 was added in large excess to 1 M copper nitrate solution containing added Se(IV), copper phosphate was precipitated and analysis of the supernatant (acidified to pH 1) indicated a Cu(II) concentration of 1-2 ppm. Analysis of the supernatant showed no evidence of Se(IV) in solution, and subsequent standard additions of Se(IV) also failed to give a peak. One ppm of Cu(II) did not severely interfere with selenium analysis in phosphate buffer at pH 1 when the Cu(II) was added to the solution at this pH. However, when it was added to the phosphate buffer at pH 6 and the solution acidified to pH 1 and analysed, interference was severe.

The interference with the selenium peak due to copper in samples of phosphate buffer may be due to formation of molecular copper phosphate at higher pH values. Incomplete dissociation of this compound, or a tendency to dissociate into ion pairs when the pH is lowered, may give rise to species at pH 1 which do not normally form at this pH, and which either react with Se(IV) or adsorb onto the surface of the gold film to prevent selenium deposition. The presence of a very small selenium peak which was almost independent of selenium concentration supports the latter

explanation. Because of the complete lack of success with the precipitation approach, it was discontinued and other methods of separating the copper were investigated.

EDTA has been used to mask interference by ions such as Cu(II) in electroanalytical methods for the analysis of Se(IV) and Te(IV) (Henze *et al.* 1969). In the present work an attempt was made to shift the copper deposition potential to more negative values by the addition of EDTA at pH 2 so that selenium would deposit selectively at the electrode without separating the Cu(II) from solution. The stripping step was carried out after transferring the electrode into 0.1 M nitric acid (referred to as 'solution exchange') to avoid interference from EDTA with the selenium oxidation peak.

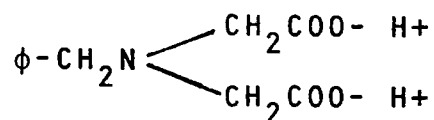
The most anodic potential at which deposition of copper occurred from a 5% solution of copper nitrate at pH 2 was -0.06 V. Upon addition of sufficient EDTA to complex 50% of the Cu(II) present, the potential moved to -0.03 V. A further addition of EDTA (3% excess of the complexing agent over that needed to complex all of the copper present) brought the threshold deposition potential back to -0.13 V, i.e. cathodic of the potential required to deposit selenium. However, subsequent analysis for selenium in this solution (employing solution exchange) failed to give any trace of a selenium peak.

EDTA is commonly thought not to complex the selenite ion, but these results indicate that some degree of complexation

does occur, sufficient to shift the selenium deposition potential to more cathodic values under the experimental conditions used. Determinations of selenium in solutions of varying EDTA concentrations supported this interpretation. Further solution exchange experiments confirmed that interference occurred during the deposition step and indicated that the EDTA interference occurred through complexation of the Se(IV) rather than by blocking the deposition of selenium by adsorption of EDTA onto the electrode surface. The EDTA approach was subsequently abandoned.

The high affinity of *Chelex 100 ion-exchange resin* for Cu(II) and the high exchange capacity for the copper tetrammine complex - quoted by the manufacturer as 0.33 millimoles (equivalent to 0.021 g of copper metal) per mL of resin - suggested the use of this resin for the ion-exchange separation of Cu(II) from dissolved copper samples. Upon dissolution and conversion to copper tetrammine, 0.5 g of copper was found to be completely retained by a column of resin (1.5 X 12 cm) in the ammonium form when eluted with 0.1 M ammonia solution. Se(IV) is completely eluted from this quantity of resin in either the ammonium or copper tetrammine form by 50 mL of 0.1 M ammonia solution. Increasing the eluent concentration to 0.5 M ammonia solution did not significantly speed up the elution of Se(IV) from the column.

Chelex 100 chelating resin is a styrene divinylbenzene copolymer containing iminodiacetate functional groups:



It is structurally classed with the weak acid cation exchangers by virtue of its carboxylic acid groups.

Chelex 100 differs from the strong sulphonic acid exchangers in its more efficient regeneration in dilute acid, and its ability to operate in basic, neutral and weakly acid solutions. The 22 mL column of resin is regenerated by running, in order, 100 mL of 2 M nitric acid, 100 mL of 0.5 M ammonia solution, and 60 mL of high purity 0.1 M ammonia solution through the column. Nitric acid desorbs the copper and ammonia solution converts the column to the NH_4^+ form. One batch of resin was used continuously for six months without a noticeable deterioration in its capacity for copper.

DEVELOPMENT OF THE ANALYTICAL METHODS

THE SELENIUM/TELLURIUM METHOD

Solutions prepared from copper nitrate were spiked with Se(IV) and Te(IV), made basic with ammonia solution, and passed through 22 mL of Chelex 100 resin. Subsequent ASV analysis of the eluent (50 mL) indicated complete (>99%) recovery of both elements, whose anodic oxidation peaks occur at +0.9 V and +0.64 V respectively (Figure 8). Neither element interfered with the determination of the other up to a concentration ratio of at least 1:5.

However, when a sample of copper metal was dissolved in nitric acid and analysed after separation, serious interference arose from two sources. First, nitrite ion produced as a reduction product during dissolution of the metal gave an oxidation wave within 20 mV of the selenium peak. It was found that the nitrite concentration had to be reduced to less than 10 ppb to eliminate this wave. Secondly, arsenic and antimony present in the copper produced oxidation peaks which interfered with the analysis of selenium and tellurium.

However, because As(V) and Sb(V) are electrochemically inactive under the conditions of ASV analysis, both of these interferences were eliminated by adding a controlled excess of hydrogen peroxide to the nitric acid digest (Hamilton *et al.* 1979a). Nitrite was oxidised to

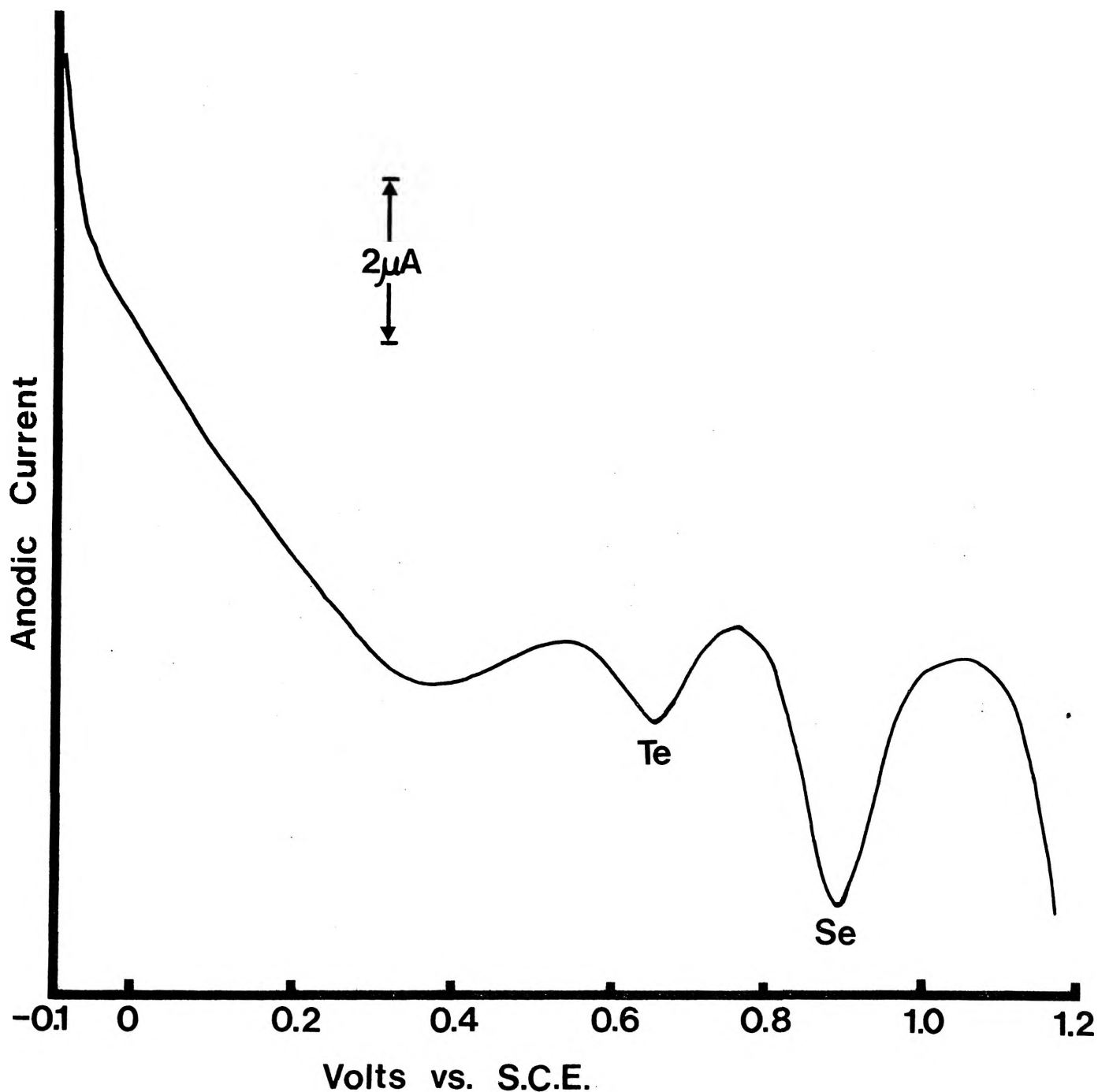


FIGURE 8 Anodic stripping current-voltage curve for 8 ppb Se(IV) and 12 ppb Te(IV); 100 s deposition at -0.1 V in 0.1 M HNO_3 , prior deposition of 2×10^{-2} coulombs of gold on the GCE.

nitrate and As(III) and Sb(III) to the pentavalent state. Oxidation of Se(IV) and Te(IV) to the electrochemically inactive Se(VI) and Te(VI) was negligible. The excess peroxide was rapidly destroyed by the catalytic activity of the high concentration of Cu(II) in solution. After only 10 min at 80-90°C, the solution could be treated with 15 M ammonia solution ready for copper removal with chelating resin.

The amounts of reagents used for the dissolution and separation are not critical. Two mL of concentrated nitric acid is sufficient to dissolve 0.5 g of copper, the resulting solution being 2 M in nitric acid. Ammonia addition results in a 2 M excess of ammonia solution, and the final addition of nitric acid to the copper-free eluate gives an acid concentration of 0.2 M.

The sensitivity of ASV analysis is influenced by a wide range of variables including deposition time, deposition potential, the range of potentials scanned (and the conditioning potential), the stirring efficiency, the surface area of the electrode, and various solution conditions including ionic strength and pH. The role of the gold film in determining electrode sensitivity has been discussed for selenium, and its effect on the tellurium peak is virtually identical.

The selenium peak height increases with increasingly negative deposition potential, from virtually zero to +0.2 V

to a limiting value at -0.2 V. A deposition potential of -0.1 V was used for optimum reproducibility. The selenium peak height also increased with deposition time (Figure 9) until the surface of the gold film neared saturation, beyond which the proportionality of peak height to selenium concentration was lost. With continued use, the area of the gold film available for selenium deposition, and therefore the point of saturation, decreased. Eventually, typically after 4 to 6 weeks of continuous use, both the linear portion of the calibration curve and the sensitivity of the electrode decreased to the extent where a new gold film was required.

During the analysis of selenium and tellurium, the deposition step was preceded by a conditioning step. During this period, the electrode was held at a potential more positive than the oxidation potential of selenium to ensure that oxidation of selenium/tellurium (and of any impurities from the electrode surface) was complete. A conditioning potential of $+1.2$ V gave the highest selenium and tellurium anodic stripping peaks while a conditioning time of 10 - 30 s led to optimum reproducibility for successive scans.

Changes in scan rate affected peak height, base line slope (caused by non-faradaic current) and to an extent, analysis time. Peak height and base line slope both increased with scan rate, although the increase in base line slope was the more pronounced of the two. A scan rate of 40 mVs^{-1} was chosen as a suitable compromise.

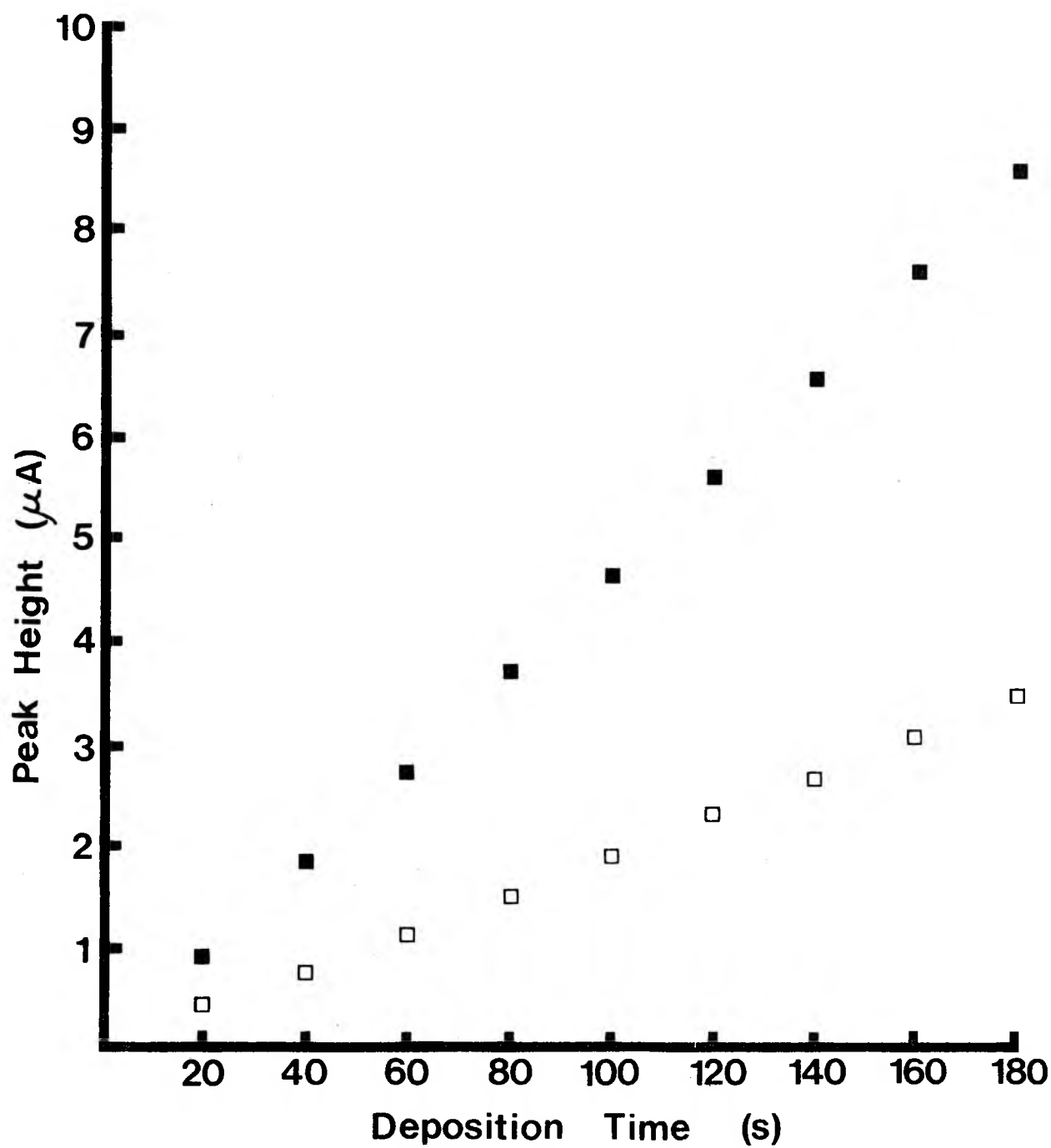


FIGURE 9 Variation of selenium and tellurium peak heights with deposition time; (■) 12 ppb Se(IV), (□) 30 ppb Te(IV); 2×10^{-2} coulombs of gold.

When the established optimum conditions were used, the absolute responses (peak height vs. concentration) for selenium and tellurium were as shown in Figure 10. These results were calculated from both peak height and peak area; no significant differences were found and peak height was used for convenience.

This procedure was used to analyse two certified samples of electrolytic copper (certified by the Spectroscopic Society of Canada and designated SSC-1 and SSC-3) for selenium and tellurium. The composition of these samples is shown in Table 2. The determination of lower concentrations of selenium and tellurium was examined by spiking solutions of duplicate samples of high purity copper metal, for which the selenium and tellurium concentrations were less than 0.1 ppm. The results of these analyses are shown in Table 3.

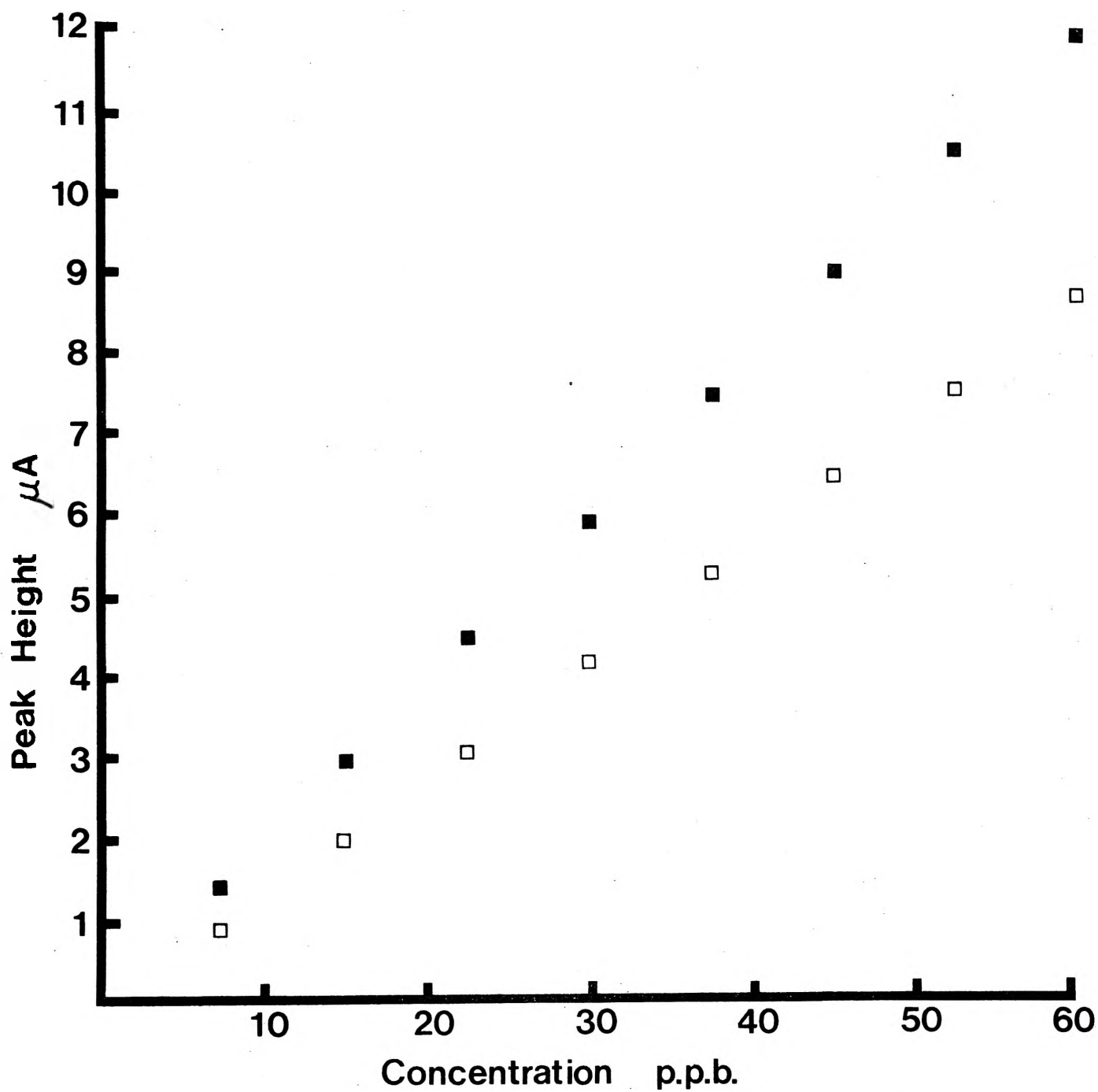


FIGURE 10 Calibration graphs for selenium and tellurium; deposition at -0.1 V in 0.1 M HNO_3 , (■) 50 s for Se(IV), (□) 160 s for Te(IV); 2×10^{-2} coulombs of gold.

TABLE 2

CHEMICAL COMPOSITION OF CERTIFIED COPPER SAMPLES SSC-1 AND SSC-3

Element	SSC-1		SSC-3	
	Recommended Value (ppm)	Standard Deviation (ppm)	Recommended Value (ppm)	Standard Deviation (ppm)
Se	7.28	1.61	3.87	0.744
Te	4.57	0.775	2.53	0.629
As	1.16	0.483	5.45	1.93
Sb	2.64	0.543	1.63	0.989
Ag	18.8	5.81	16.1	3.59
Bi	1.15	0.325	0.59	0.012
Cd	N.F. ^a	-	N.F.	-
Fe	39.2	7.18	40.0	8.82
Ni	17.6	3.36	48.0	7.68
Pb	65.3	7.02	4.58	1.51
S	19.6	6.79	16.7	8.93
Sn	54.9	6.70	12.0	1.68
Zn	33.3	7.91	15.3	3.60

^aNot Found

TABLE 3

DETERMINATION OF SELENIUM AND TELLURIUM IN COPPER

Element	Sample	As or Sb ($\mu\text{g g}^{-1}$)	Concentration added ($\mu\text{g g}^{-1}$)	Concentration found ($\mu\text{g g}^{-1}$)	Recovery (%)	R.s.d. (n=5) (%)
Se	SSC-1 ^a	7.28	-	7.80	107.2	1.6
	SSC-3 ^a	3.87	-	4.24	109.6	1.5
	Copper	0.07	2.25	2.34	100.8	1.4
	Copper	0.07	1.20	1.28	100.8	3.6
	Copper	0.07	0.50	0.58	101.7	3.7
	Blank	-	-	0.06	-	5.8
Te	SSC-1	4.57	-	4.55	99.5	2.3
	SSC-3	2.53	-	2.65	104.8	1.8
	Copper	<0.02	1.50	1.48	98.7	2.6
	Copper	<0.02	2.25	2.28	101.4	1.6
	Copper	<0.02	0.50	0.50	100.0	3.1
	Blank	-	-	<0.02	-	-
	Blank + added Te	-	0.10	0.10	100.0	7.3 ^b

^aCertified values are 7.28 ppm Se and 4.57 ppm Te for SSC-1 and 3.87 ppm Se and 2.53 ppm Te for SSC-3.

^bn=10.

Anodic stripping voltammetry with the gold-film electrode gives a detection limit of 0.1 ppb (1.3×10^{-9} M) selenium and 0.2 ppb (1.6×10^{-9} M) tellurium in solution. The detection limits were calculated as $2\sqrt{2}$ the standard deviation of the blank (blank plus 0.1 ppm in the case of tellurium). They correspond respectively to 0.01 and 0.02 ppm in copper because 0.5 g of copper gives 50 mL of solution. Relative standard deviations ($n=5$) ranged from 1.4 to 3.7% for selenium concentrations of 7.3-0.6 ppm in copper and from 1.6 to 3.1% for tellurium concentrations of 4.6-0.5 ppm. R.s.d. figures were obtained by dissolving 5 separate samples, analysing each final solution twice, and averaging the two analytical results. The time required for the dissolution and separation was 30 min, with a further 20-100 min for the subsequent analysis, depending on the deposition time required.

No interference effects were found from 10 ppm of the following elements in copper: silver, cadmium, nickel, lead, tin, zinc, sulphur, iron, bismuth and manganese. These concentrations exceed those normally found in electrolytic copper.

THE ARSENIC/ANTIMONY METHOD

In dissolving copper in nitric acid prior to the analysis of arsenic and antimony, two problems arose: partial oxidation of arsenic and antimony to the V state, and the generation of nitrite which interfered with electrode response in the final voltammetric analysis.

As(V) and Sb(V) are electrochemically inactive in the range of potentials available with a gold electrode, and so reduction to the III state was necessary before analysis. Reducing agents such as potassium iodide, cuprous chloride and hydrazine sulphate are unsuitable because excess reductant or byproducts of the reduction reaction interfere with the ASV determination. Reduction of As(V) to As(III) with sodium sulphite in solutions of high acidity has been reported (Buldini 1979; Henry *et al.* 1979) and was found to work well for Sb(V) and As(V) in high concentrations of sulphuric acid. A trial reduction of As(V) with sulphite in sulphuric acid (4 M) in the presence of cupric ions (0.1 M) brought about partial reduction of Cu(II) to Cu(I) and gave incomplete reduction of As(V). The reduction must therefore be carried out after separation of cupric ions from the sample.

Both problems were overcome by adding a few millilitres of sulphuric acid to the eluate from the ion exchange column and then boiling down to sulphuric acid fumes before adding the sodium sulphite (Hamilton *et al.* 1980). This

procedure removed nitrite, and also nitrate which would otherwise be reduced by the sulphite. Reduction of arsenic and antimony from the V to the III state was better than 97%. Addition of sodium sulphite solution to the sample requires some care; it results in rapid evolution of sulphur dioxide and some violent sputtering may occur if the sample solution is too hot. On the other hand, if the sample solution or the sulphite solution is not hot enough, crystallisation of sodium sulphate will occur and may occlude some As(V) or Sb(V). Traces of sulphur dioxide remaining in the solution after the sample preparation are quickly driven off during the initial purge of the analysis step.

Elution of arsenic and antimony in both the III and V oxidation states through a Chelex 100 column containing bound copper tetrammine complex was examined. Both elements in each oxidation state were quantitatively eluted under the conditions described.

The potentials of the stripping peaks for both arsenic and antimony occur at about +0.18 V and are shown in Figure 11. Peak overlap is severe. The potentials of the stripping peaks are independent of the deposition potential and are shown at various pH values in Table 4.

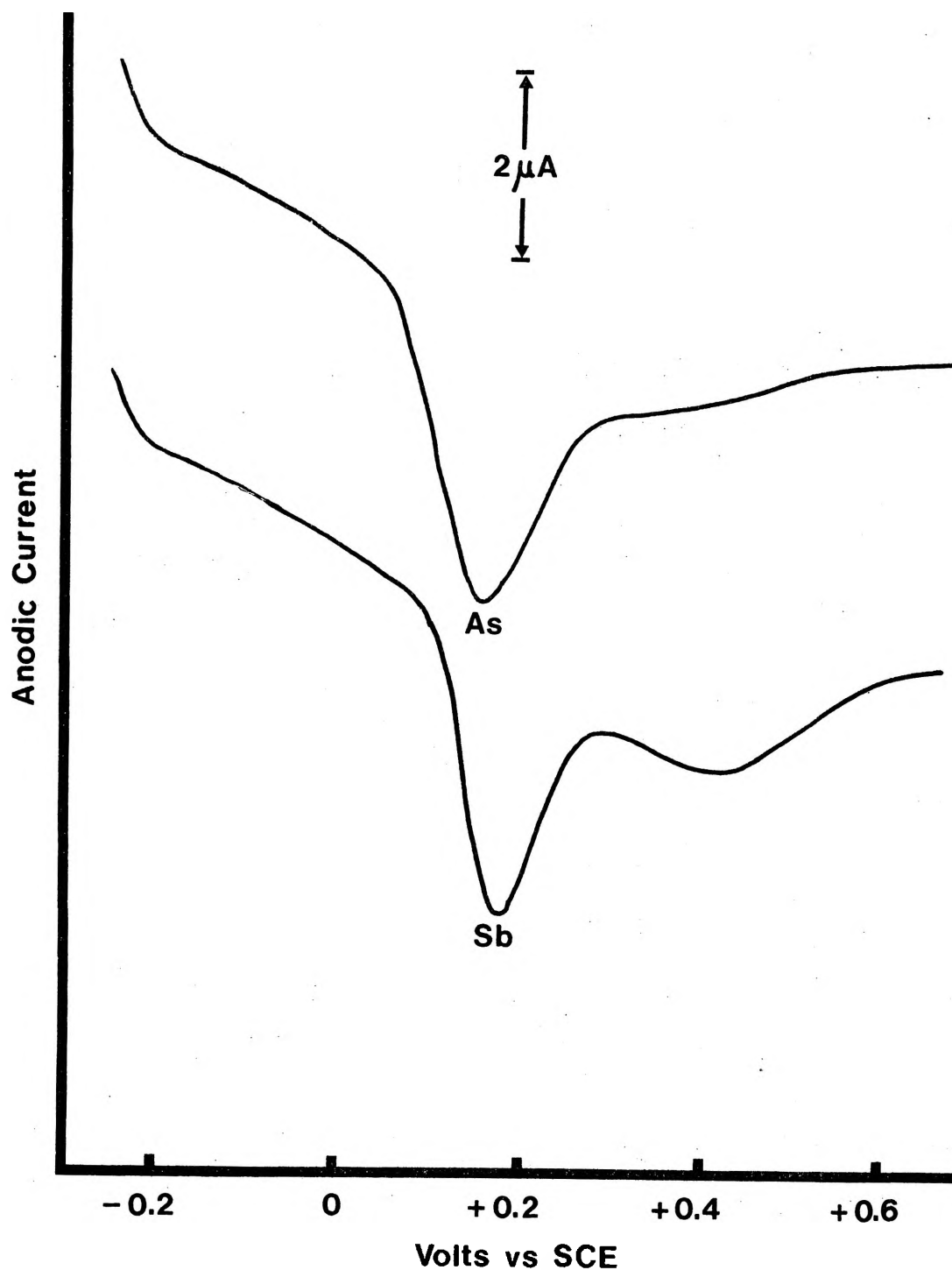


FIGURE 11 Anodic stripping current-voltage curves for 15 ppb As(III) and 13 ppb Sb(III); 200 s deposition at -0.35 V in 1 M H₂SO₄, prior deposition of 2×10^{-2} coulombs of gold on the GCE.

TABLE 4

THE POTENTIAL OF STRIPPING PEAKS FOR ARSENIC AND
ANTIMONY AT A GOLD-FILM ELECTRODE; scan rate 40mVs⁻¹

pH	0	1	2	4.5	6.5 ^a
As	+0.18	+0.18	+0.175	+0.04	-
Sb	+0.20	+0.185	+0.175	+0.03	-

^a No peaks were obtained at a deposition potential of -0.25 V.

Sulphuric acid was used for pH 0 and 1.0 and phosphate buffers for pH 2.0-6.5. All attempts to achieve separation of the oxidation potentials of arsenic and antimony by altering the solution conditions and electrolyte composition were unsuccessful, as were attempts to selectively reduce one of the elements to the hydride with various reducing agents. In particular, the Fleitmann test (selective reduction of arsenite to arsine by aluminium/aqueous sodium hydroxide) was not effective at the concentration levels of arsenic and antimony encountered in this study; antimony(III) was also reduced, probably to the elemental state, and could not be easily re-oxidised to the III state. Selective reduction with borohydride under nitrogen showed the most promise but the separation was no better than 80%, with Sb(III) being preferentially reduced. The presence of dissolved oxygen raised the efficiency of borohydride reduction of both As(III) and Sb(III). For example, reduction of 100 ppb of As(III) was

found to be hundreds of times more efficient in solutions open to the atmosphere than in similar solutions purged free of oxygen with a continuous stream of nitrogen. Selective reduction from the V state to the III state did not look promising and attempts to selectively oxidise one of the elements from the III to the V state were unsuccessful.

A solution to the problem lay in selective electro-deposition (Figure 12). By applying -0.05 V to the gold-film electrode during the deposition step, antimony is deposited from sulphuric acid solution whereas arsenic is not. The resultant stripping peak height is therefore determined only by the antimony concentration. By adjusting the deposition potential to -0.30 V, both antimony and arsenic are deposited and the resulting stripping peak enables the calculation of arsenic concentration by difference. The deposition potential of -0.30 V was chosen because the electrode response to arsenic and to antimony was found to be the same for both elements at that potential, thus simplifying the standard addition procedures and the final calculations.

In addition to the deposition potential, the sensitivity of the analysis is also affected by conditioning potential, conditioning time, scan rate, solution stirring efficiency and the condition of the gold film. The effect of gold-plating conditions on deposition efficiency has been discussed and applies equally to this work. Peak heights increase with deposition time (Figure 13) until the surface

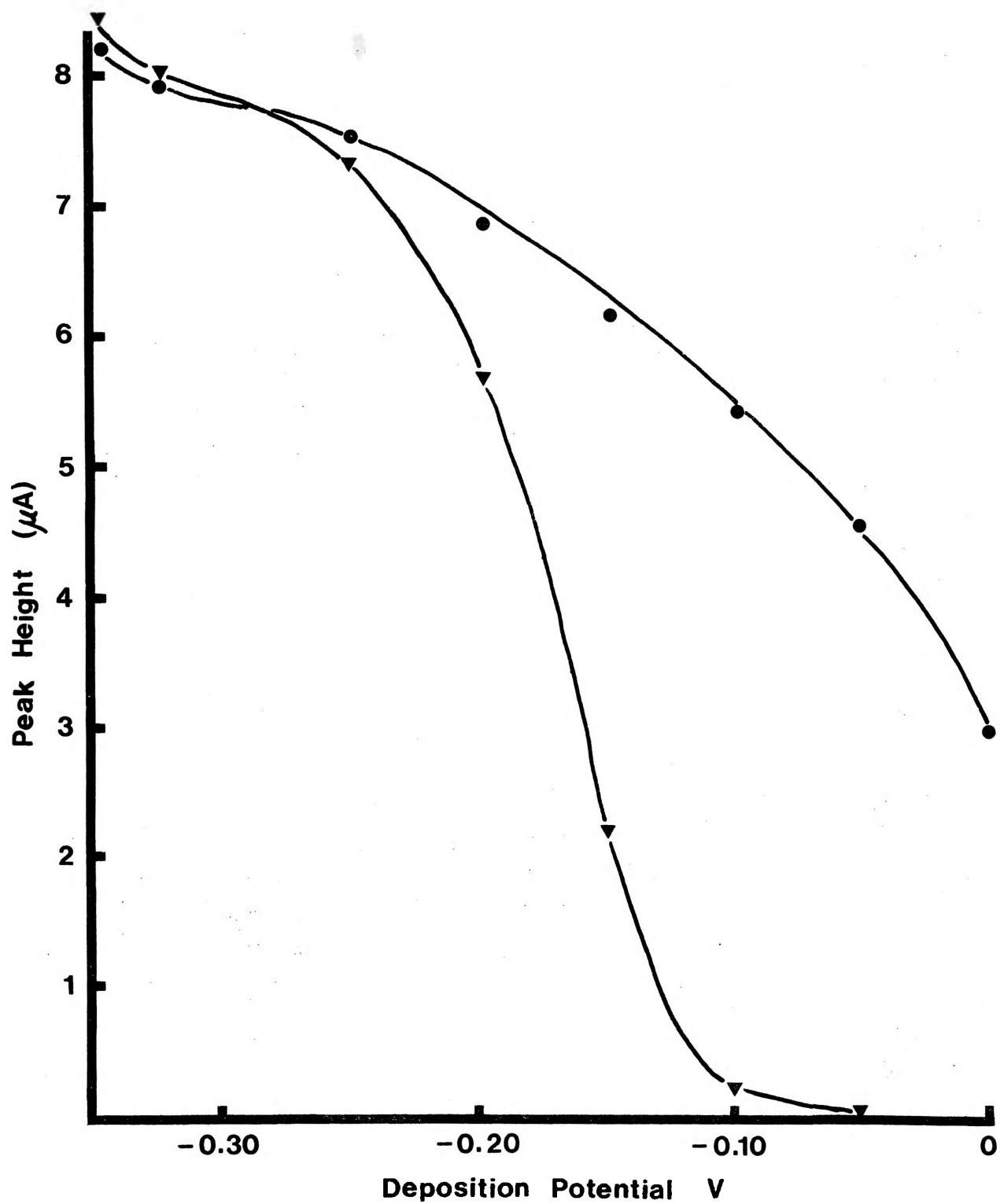


FIGURE 12 Peak height versus deposition potential for 33 ppb As(III) (▼) and 33 ppb Sb(III) (●); deposition time 200 s.

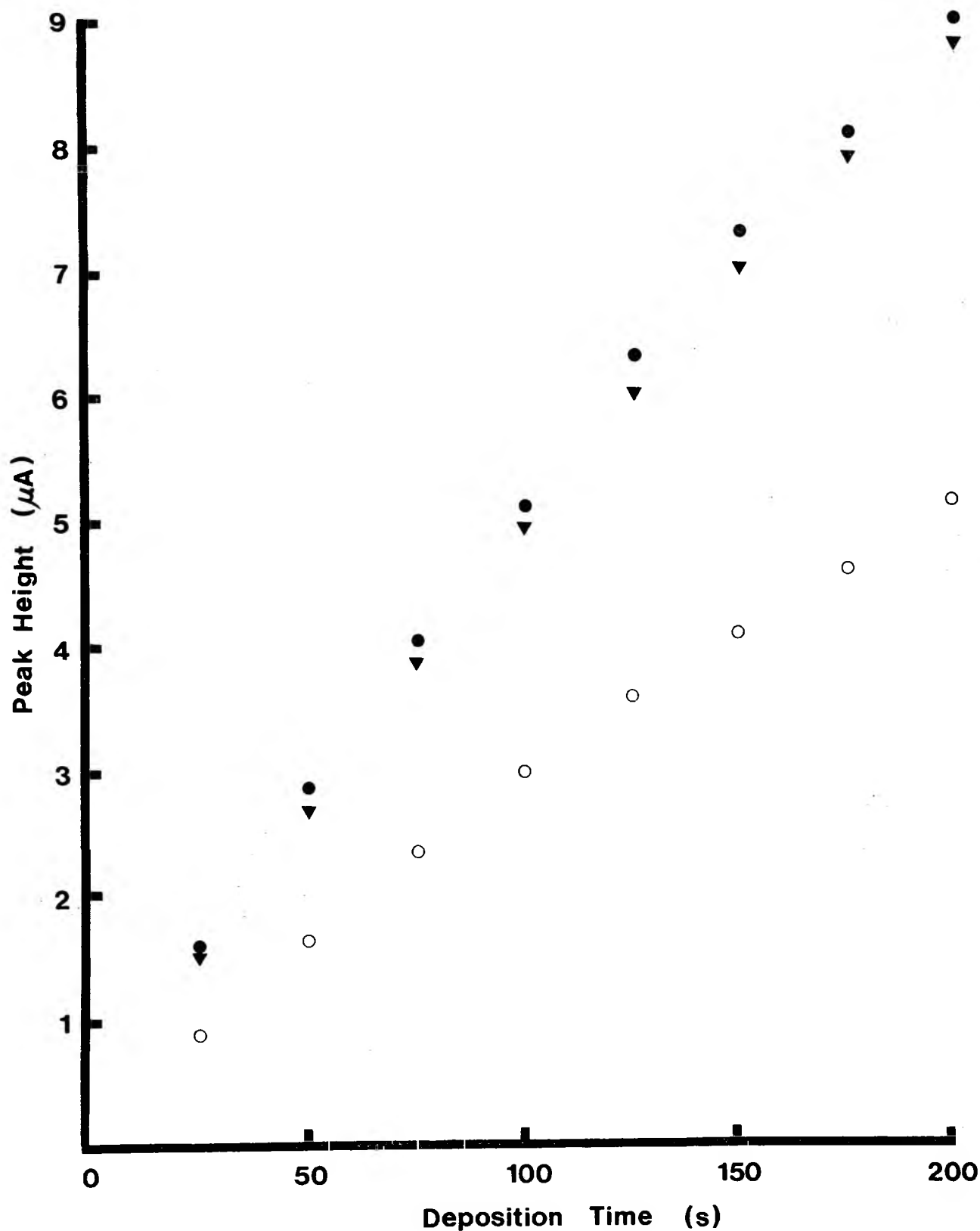


FIGURE 13 Variation of arsenic and antimony peak heights with deposition time; (\blacktriangledown) 45 ppb As(III), (\bullet), (\circ) 45 ppb Sb(III); deposition potential -0.30 V (\blacktriangledown), (\bullet) and -0.05 V (\circ); 2×10^{-2} coulombs of gold

of the gold film nears saturation, beyond which the proportionality of peak height to concentration is no longer obeyed.

A positive conditioning potential is applied to the electrode prior to the deposition step to ensure an electrochemically reproducible surface for deposition. A conditioning potential of +0.9 V gave the most reproducible arsenic and antimony stripping peaks while the optimum conditioning time was 20-30 s. A scan rate of 40 mVs^{-1} represented a suitable compromise between peak height and baseline slope. Using these parameters, the absolute responses (peak height versus concentration) for arsenic and antimony are as shown in Figure 14. These results were calculated from both peak height and peak area and although peak area gave slightly more accurate results, the differences were not great and so peak height was used for convenience.

Two certified samples of electrolytic copper (certified by the Spectroscopic Society of Canada, and designated SSC-1 and SSC-3) were analysed for arsenic and antimony. The composition of these samples is shown in Table 2. The determination of lower concentrations of arsenic and antimony was examined by spiking solutions of duplicate samples of high purity copper. The results are shown in Table 5. The relatively high blanks were due principally to impurities in the sodium sulphite used and could possibly be lowered by using sulphur dioxide gas in place of sodium sulphite. The method of determining arsenic concentration by difference

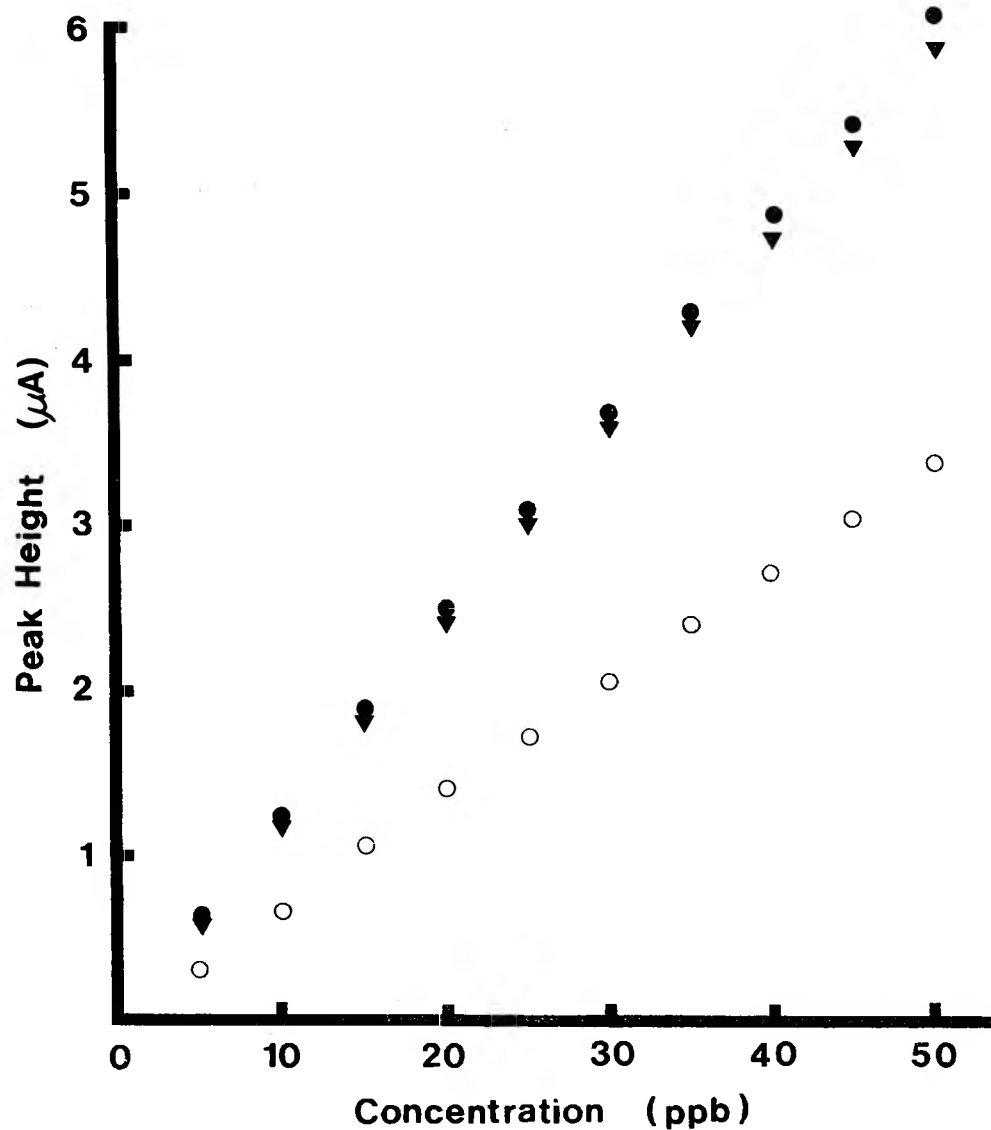


FIGURE 14 Calibration graphs of arsenic and antimony; deposition in 1 M H_2SO_4 at -0.30 V for As(III) (▼) and -0.30 V (●), -0.05 V (○) for Sb(III); deposition time 100 s; 2×10^{-2} coulombs of gold.

resulted in the relative standard deviations for arsenic being significantly higher than for antimony when the two elements were present in similar concentrations.

The limits of detection were calculated as $2\sqrt{2}$ the standard deviation of the blank. This gives a limit of detection in solution of 0.56 ppb (4.6×10^{-9} M) for antimony and 1.12 ppb (1.5×10^{-8} M) for arsenic. These limits correspond respectively to 0.028 and 0.056 ppm in copper because 0.5 g of copper gives 25 mL of solution. Each r.s.d. figure was obtained by dissolving five separate copper samples and analysing each final solution only once; around 35% improvement in detection limit is realised by duplicating the final analysis and averaging the two analytical results. The time required for the dissolution and separation was 30 min. The electrochemical analysis required 20 min excluding the preliminary purge and allowing a deposition time of 3 min. A single gold film can be used for more than 200 determinations before declining sensitivity requires repolishing of the GCE and deposition of a new gold film.

No interference was caused by 10 ppm of the following elements in copper: silver, cadmium, nickel, lead, tin, zinc, sulphur, iron, bismuth and manganese. These concentrations exceed those normally found in electrolytic copper.

TABLE 5

DETERMINATION OF ARSENIC AND ANTIMONY IN COPPER

Element	Sample	As or Sb ($\mu\text{g g}^{-1}$)	Concentration added ($\mu\text{g g}^{-1}$)	Concentration found ($\mu\text{g g}^{-1}$)	Recovery (%)	R.s.d. (n=5) (%)
As	SSC-3 ^a	5.45	-	5.44	100	6.1
	SSC-1 ^a	1.16	-	1.29	111	15.0
	Copper	0.05	1.0	1.12	107	11.9
	Copper	0.05	0.5	0.52	95	12.1
	Blank	-	-	0.12	-	17.8
Sb	SSC-3	1.63	-	1.61	98.5	6.8
	SSC-1	2.64	-	2.75	104	4.1
	Copper	<0.03	1.0	0.97	97	5.5
	Copper	<0.03	0.5	0.48	95	6.9
	Blank	-	-	0.06	-	15.2

^aCertified values are 5.45 ppm As and 1.63 ppm Sb for SSC-3
and 1.16 ppm As and 2.64 ppm Sb for SSC-1.

CONCLUSION

Compared with other methods of analysis, the ion exchange-ASV procedure for the determination of selenium, tellurium, arsenic and antimony offers advantages in terms of simplicity, sensitivity, specificity and cost effectiveness. It requires no special apparatus beyond basic d.c. ASV equipment. The use of the gold-film electrode avoids the cost of a solid gold electrode, enabling the facile preparation of a fresh surface by polishing and electro-deposition of gold should there be contamination of the working electrode.

The method is rapid and well suited to routine analysis. It requires only a small sample weight and very small amounts of reagents each of which can be easily obtained in highly pure form. One advantage of the method which is unmatched by any previously published is that the separation of copper from the sample is quantitative.

The sensitivity of the ASV analysis method can be increased still further by using an electrode with a larger surface area, switching to a rotating working electrode to increase mass transport over the electrode surface, and by the use of derivative signal processing. The sensitivity of the arsenic/antimony analysis could be increased simply by using sulphur dioxide gas or purer sodium sulphite to lower the blank value.

Although the matter was not pursued here, the work described in this chapter raises the possibility of finding quantitative electroanalytical methods for a variety of species including Cu(II) , NO_2^- , H_2O_2 , and ferrocyanide and ferricyanide (in the presence of Cu(II) or Zn(II)), all of which give sensitive anodic waves or peaks at the gold electrode.

Chapter 5

AN AUTOMATIC CONTROLLER FOR VOLTAMMETRIC ANALYSIS

INTRODUCTION

In the past decade we have witnessed a sudden increase of interest in electroanalytical techniques. This is due, in large part, to the availability of greatly improved electrochemical instruments. The next progression would seem to be system automation which offers speed, accuracy and reproducibility of analysis not available with manual operation. Automation also allows streamlining of analytical operations and frees the chemist from the mundane repetitive work of switching and adjusting instruments during an analysis.

The design of the automatic controller (Hamilton *et al.* 1979) incorporates many of the features of commercial instruments available for automated electroanalysis (such as the EG & G *Princeton Applied Research* PAR-315 Automated Electroanalysis Controller and PAR-374 Microprocessor-based Polargraphic Analyser) but has extended capability and/or flexibility in the following areas: number of deposition-scan cycles run under automatic control; choice of times for individual steps; variable recorder offset; provision for a pre-deposition step; and function overrides. The automatic controller described here has been designed specifically to extend the capability of the P.A.R.C. instrumentation available to this laboratory. It is easy to operate, relatively simple in construction and inexpensive to build; its external dimensions are the same as the PAR-174.

DESCRIPTION OF THE CONTROLLER

The automatic controller is basically an accurate programmable timer which is capable of activating a number of relays, switches and voltage sources, both within and external to the controller, as programmed by the operator. It has been designed specifically to operate in conjunction with the PAR-173 Polarographic Analyser, PAR-175 Universal Programmer, PAR-173 Potentiostat/Galvanostat, *Houston* 2000 series X-Y Recorder and several pieces of ancillary apparatus consisting of a magnetic stirrer, *Beckman* Rotating Electrode Assembly, millivoltmeter, three-electrode cell system and a supply of nitrogen (Figure 15).

Besides its controlling function, the controller acts also as a signal switching unit enabling maximum versatility when using the described equipment together. Figure 16 is a simplified block diagram of the electrochemical system in which the controller is used. The controller uses digital logic to automatically initiate solution purging, electrode pre-deposition and up to sixteen deposition-scan cycles with automatic recorder offset after each cycle. The exact time of an analysis step can be programmed and any particular step may be bypassed altogether. The electrode conditioning voltage is generated by the controller. Relay/switch overrides and selected function overrides are also provided and a number of front panel lights are incorporated to indicate the operational mode of the controller.

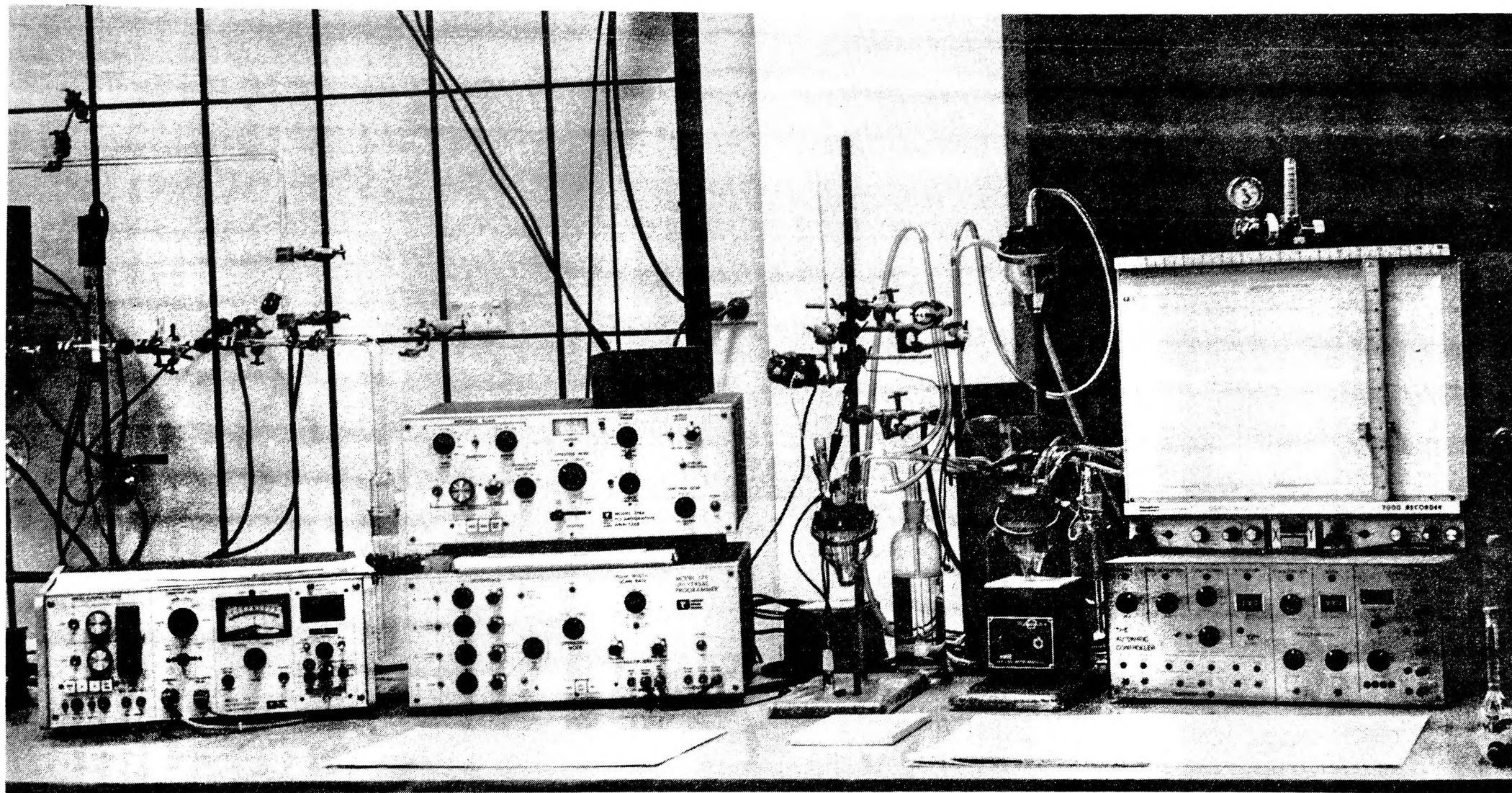
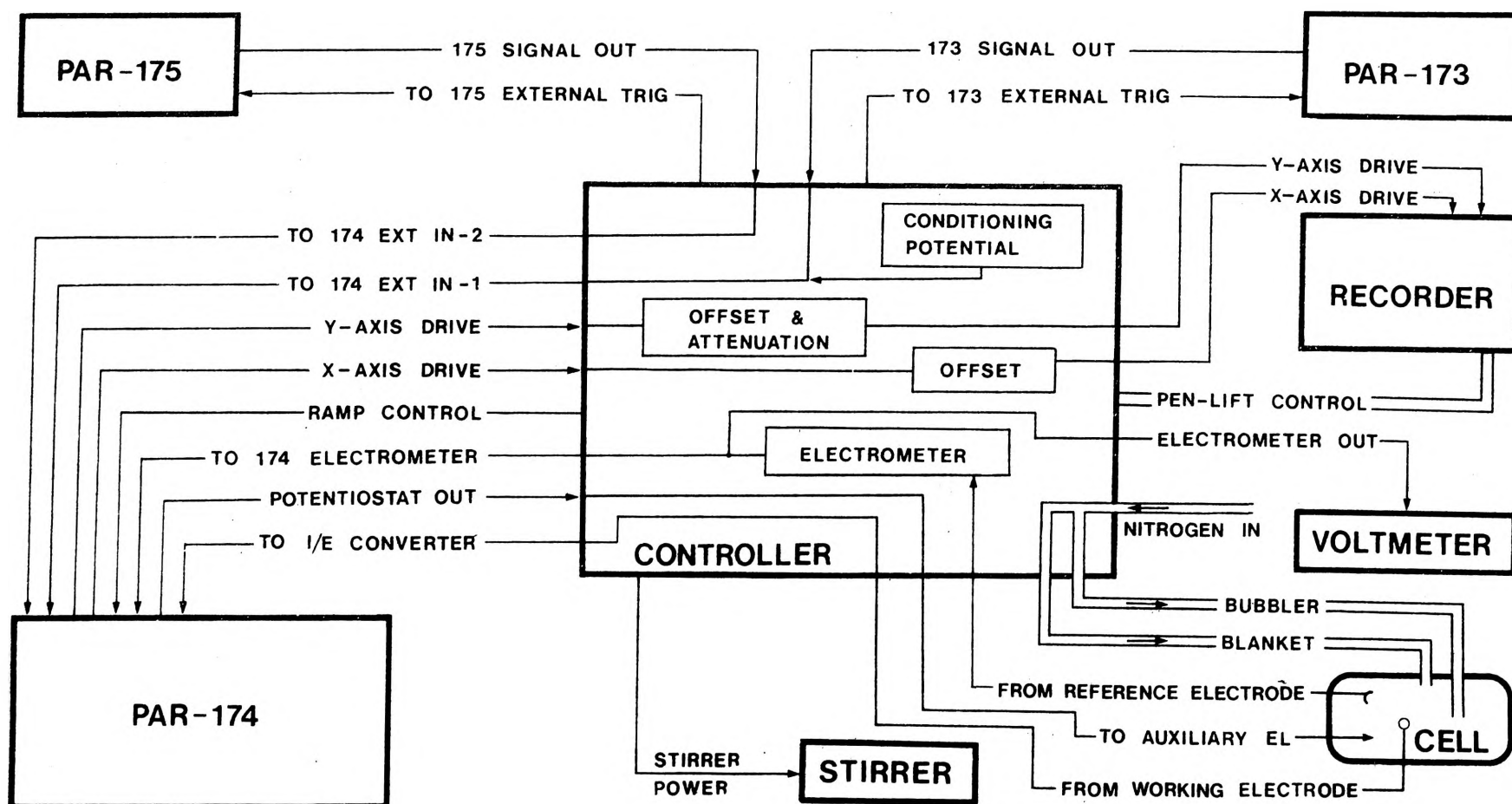


FIGURE 15 The Electrochemical System used by the Author.

The Automatic Controller is underneath the X-Y Recorder.

FIGURE 16 Simplified Block Diagram of the Electroanalytical System.



OPERATIONAL SEQUENCE

The controller is designed to function in seven stages: stand-by, purge, pre-deposition, conditioning, deposition, equilibration and scan. The last six stages are referred to as analysis steps. Each stage is accompanied by a front-panel status light. The status of the principal controller relays and switches during each of these stages is shown in Figure 17 and is described below.

When initially powered (and upon completion of an analysis) the controller is in *stand-by* mode during which the stirrer is off, the auxiliary electrode is disconnected, and the blanketing nitrogen is applied to the cell solution to prevent oxygen contamination. The voltage sources are in 'INIT' mode.

Upon pressing the 'START' button the first analysis cycle begins with the *purge* step during which nitrogen is bubbled through the cell solution to drive out dissolved oxygen. All other relays/switches are unchanged. The controller remains in this step for the programmed time, after which it jumps to the pre-deposition step.

On entering the *pre-deposition* step, nitrogen is switched to the blanketing tube (to direct a blanket of nitrogen over the solution surface), the stirrer is switched on and the auxiliary electrode is connected. The voltage source remains in 'INIT' mode. The pre-deposition step was

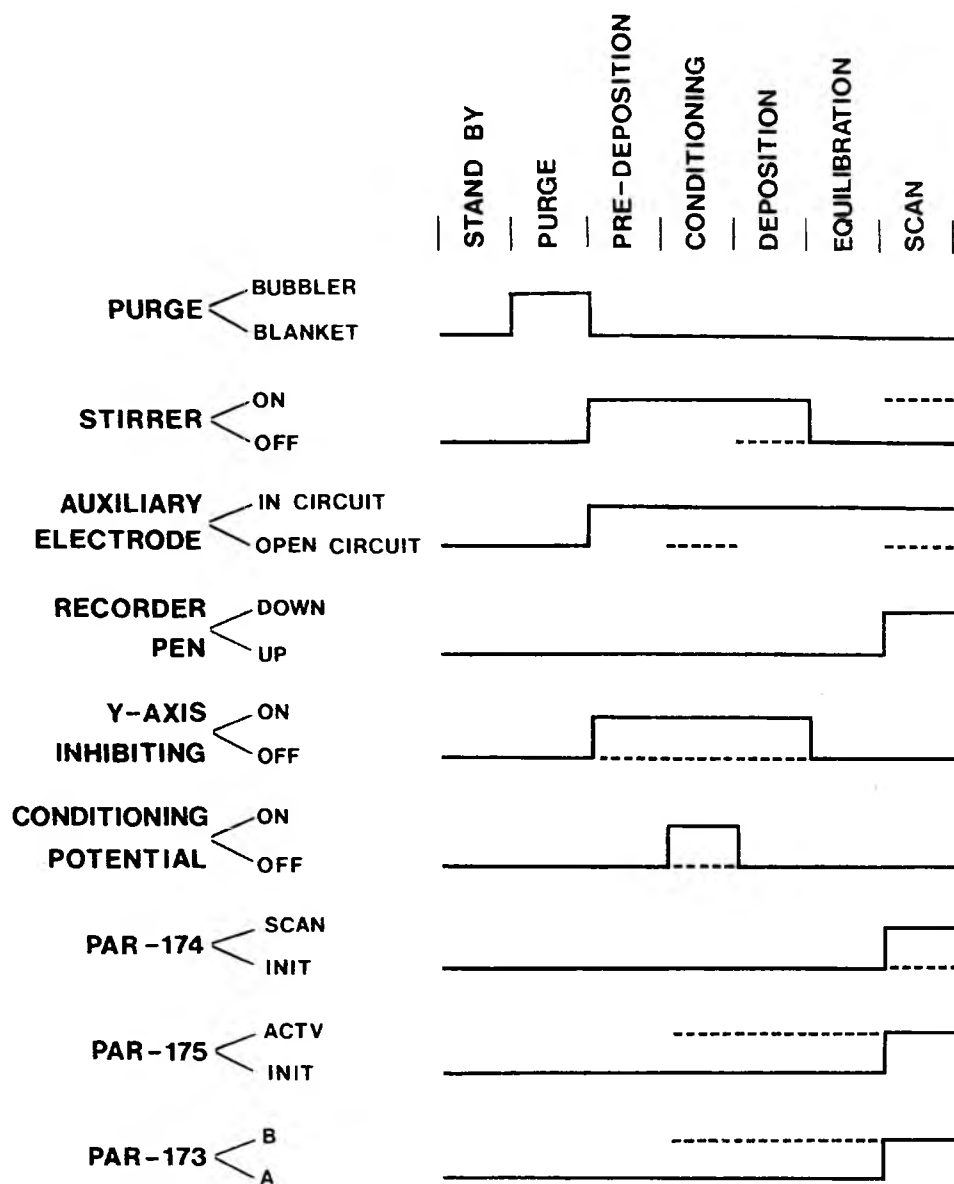


FIGURE 17 Timing Diagram.

(Broken lines indicate function overrides)

included because of its importance in work using thin mercury-film electrodes (Florence 1970). The purge and pre-deposition steps are used only in the first cycle; second and subsequent cycles begin with the next analysis step, namely conditioning.

When the controller enters the *conditioning* step, the conditioning potential offset generated by the controller is applied to the cell. The conditioning potential is set as required to electrochemically 'clean' the working electrode. Also, the Y-axis drive is inhibited to reduce wear and tear on the recorder.

The *deposition* step follows next and the conditioning potential offset is removed. During this step, the various species of interest deposit on the working electrode.

Upon entering the *equilibration* step, the stirrer is switched off and the Y-axis drive inhibiting ends, and the cell solution is left to quiesce.

The final step is the *scan*. The voltage source is switched to 'SCAN' ('ACTV' in the case of the PAR-175), the recorder pen is lowered and the generated voltage ramp is applied to both the cell and the X-axis input of the recorder to linearly deflect the pen along the X-axis. (Alternatively, the same result is obtained by applying the controller electro-meter output to the X-axis input). When the voltage at the working electrode reaches the characteristic reaction potential of each species on the electrode, each is oxidised/reduced back

into solution, producing a current peak. This current is converted to a voltage and applied to the Y-axis input of the recorder.

Upon conclusion of the scan step, the cycle count is incremented by one, and either of two things can happen according to the programming. If the cycle count equals the number of cycles programmed, the controller will enter standby mode and remain there indefinitely. Otherwise, the voltage source will be set to 'INIT', the controller will return to the conditioning step and all relays will return to the state previously described for that step; the recorder pen lifts, the stirrer is switched off, Y-axis inhibiting returns and the conditioning potential is applied. Also the X and/or Y-axis drives will be offset as programmed so that subsequent voltammograms will not obscure one another, and the next analysis cycle will have commenced.

Depending on the electroanalytical technique involved, one or more of these analysis steps may be omitted by setting the timing control for that step to its minimum setting. ASV and CSV with thin mercury-film electrodes plated *in-situ* will probably involve all six analysis steps, although use of a hanging mercury drop electrode or a solid electrode would not necessitate the pre-deposition step. Polarography with the dropping mercury electrode would involve only the purge and scan steps. Thus an analysis requiring from one to sixteen cycles can be run without operator attention (unless spikes of standard or other solutions need to be manually introduced during the analysis).

TIMING CONTROLS

The length of time that the controller remains in each analysis step is programmed by setting the corresponding timing control. Multiposition rotary switches are used for the purge (1, 100, 200, 500 & 1000 s), pre-deposition (0, 100, 200, 500 & 1000 s), conditioning (0, 10, 20, 30, 60, 100, 200, 500 & 1000 s) and equilibration (1, 10, 20, 30 & 60 s). Three digit decimal thumbwheel switches adjustable from 0 to 999 s in 1 s increments, are used for the deposition and scan steps. For convenience, all times are in seconds. These, and all other controls on the controller may be set or changed at any time during an analysis cycle with immediate effect.

OVERRIDES AND CONTROL SWITCHES

Two types of overrides are available *i.e.* direct and function overrides. *Direct overrides* (toggle switches - front panel) allow operator control of the purge valves, stirrer, connection of the auxiliary electrode, and lowering of the recorder pen. Each can be switched to 'AUTO', 'ON' (purge valves direct gas to the bubbler tube), and 'OFF' (purge valves direct gas to the blanketing tube). Overrides are also available to switch the PAR-174 and PAR-175 between 'INIT' and 'SCAN' ('ACTV' on the PAR-175) mode.

The *function overrides* (toggle switches - rear panel) are illustrated by broken lines in Figure 17 and can be used to reprogram selected controller functions. They can be

used, for example, to disable the Y-axis inhibiting, or to program the controller to disconnect the auxiliary electrode during the scan and conditioning steps as would be required for potentiometric stripping analysis (Jagner & Graneli 1976). In addition to those shown in Figure 17, two extra overrides are available; one disconnects the scan timing control, allowing a scan of longer than 999 s as may be required for potentiometric stripping analysis, and the other doubles the X-axis offset voltage when using the recorder at reduced sensitivity on that axis.

The pushbutton *control switches* on the front panel of the controller facilitate system control. Besides the 'START' button (which initiates the first cycle) and the 'FINISH' button (which immediately deactivates all relays, resets the cycle count and returns the system to stand-by mode), push-buttons are provided which enable the operator to restart the current analysis cycle; hold the controller in its present step indefinitely; jump the controller immediately to the next step; and restart the cycle count and consequently cancel the accumulated offset voltage(s) applied to the recorder.

The *clock readout* is a 3 digit 7 segment light-emitting diode display showing elapsed time for each step and is accompanied by the clock reset button. The front and rear panels of the controller are pictured in Figures 18 and 19.

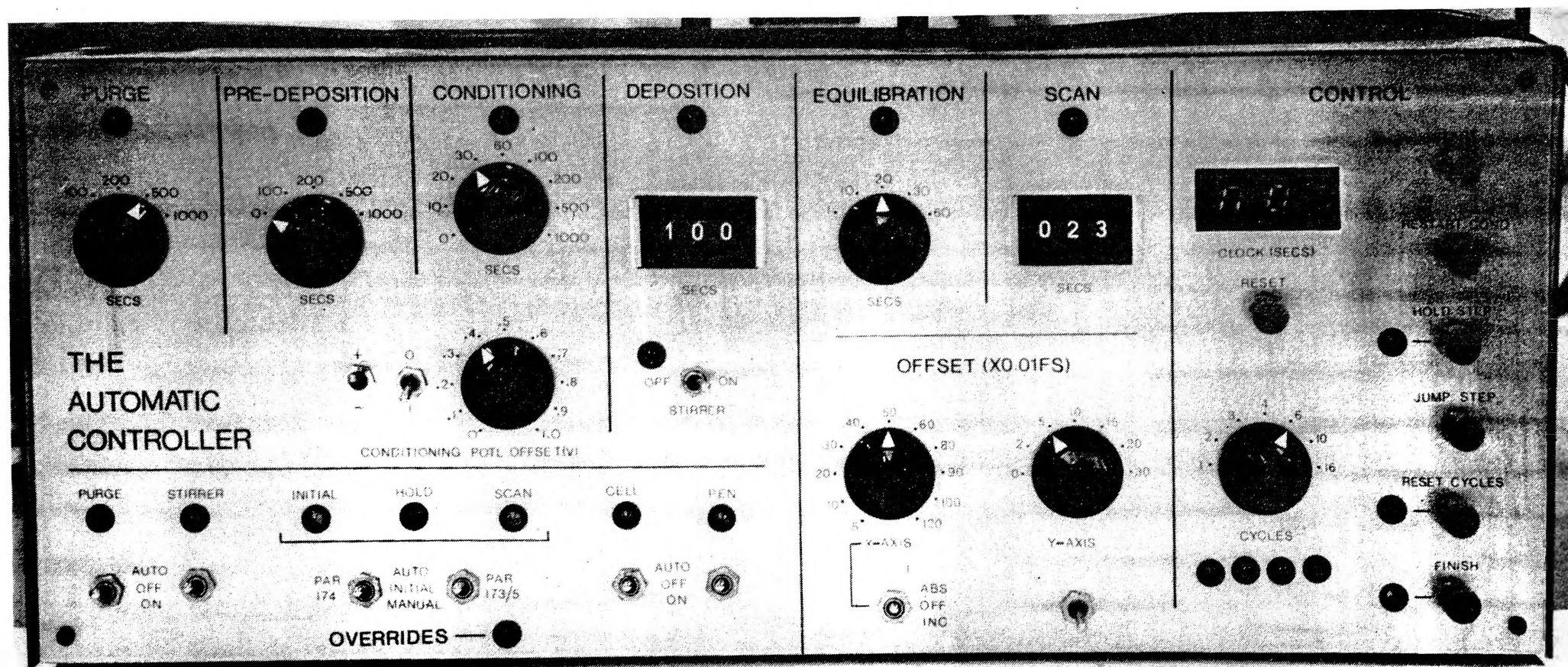


FIGURE 18 The Controller - Front Panel.

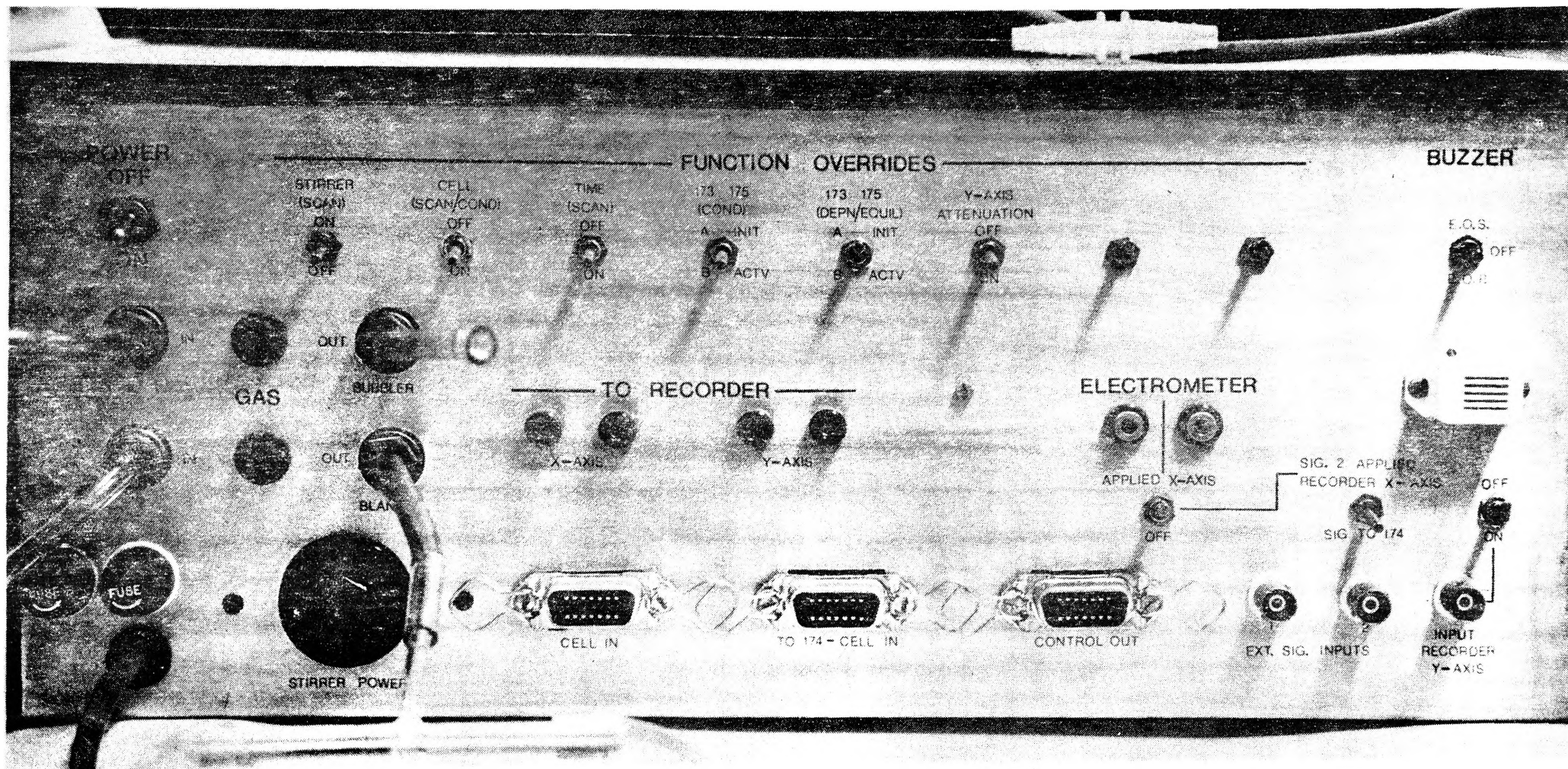


FIGURE 19 The Controller - Rear Panel.

INTERNAL VOLTAGE SOURCES

The controller incorporates three internal voltage sources: the conditioning potential offset, X-axis offset and Y-axis offset. The conditioning potential offset is summed with the 'INIT' potential from the external voltage source to give the required electrode conditioning potential. The offset is adjusted to 100 mV increments from -2 V to +2 V. The multiposition switch controlling the Y-axis offset may be set to ± 0.00 , 0.02, 0.05, 0.10, 0.15, 0.20 or 0.30 times full scale on the Y-axis of the recorder. At the conclusion of each scan step, the Y-axis offset applied to the recorder is incremented by the amount shown on this switch.

The X-axis offset is also adjustable with 12 settings between 0 & 1.2 times full scale. This offset can be switched to function in one of two ways: (a) the offset works in an identical manner to the Y-axis offset, or (b) upon selecting the offset required, the recorder's X-axis is immediately offset by the amount shown on the multiposition switch and no subsequent incrementation occurs.

ELECTROMETER

A LN0042 operational amplifier/voltage follower ($>10^{12} \Omega$ input impedance) was used to build a high performance electrometer to follow the voltage at the working electrode (with respect to the reference electrode) and give a continuous buffered output identical (± 0.5 mV) to the working electrode voltage.

OTHER FEATURES

A number of *status lights* (individual light-emitting diodes) are included in the front panel. These lights indicate which analysis step is in progress, advise the state of each of the main relays/switches (*i.e.* purge, stirrer, auxiliary electrode connection, recorder pen and PAR-174 & PAR-175 mode), advise when selected overrides are in operation, display the cycle count and indicate the state of some of the pushbutton control switches. The cycle count is displayed in binary using 4 light-emitting diodes. A multiposition switch is provided that sets the number of cycles to be automatically completed. This switch gives the operator the choice of running 1, 2, 3, 4, 6, 10 or 16 cycles automatically.

A solid state *buzzer* on the rear panel can be switched so that (a) it sounds for 1 s during every even numbered scan, or (b) it sounds at the end of every deposition step. The former is useful, for instance, when an operator is required to add spikes of a standard solution to a sample during an analysis; the buzzer sounds to remind the operator that two cycles have been completed and that a standard addition may be due. The latter is useful when the operator is required to make a change to the cell between the deposition and scan steps, such as exchanging solutions or electrodes when using solution exchange techniques. When not required, the buzzer is switched off.

SYSTEM CHARACTERISTICS

A simplified schematic overview of the controller is shown in Figure 20. In the paragraphs that follow, the controller circuitry is discussed in a general way from the point of view of function and relationships between functions shown in the block diagram.

The power supply generates four regulated supply voltages; +5 and -5 V for CMOS logic and +12 and -12 V for other circuitry.

The *clock* timing (A) is based on 50 cycles mains frequency. This is divided to give 1 hz., then divided further to give decimal coded lines for use with the timing switches. The *timing switches* (B) are connected such that, for each state, when the set time interval registers on the clock, the output from that state goes 'on'.

The outputs from the time switches are connected to a 1 of 8 channel data selector (C). This uses the current state number to enable one of its input lines to be connected to its output line i.e. it chooses which time switch is to be monitored. When a positive signal comes through from a time switch via the 1 of 8 channel data selector this indicates it is time to change states; the *state counter* (D) is changed to a new value and the clock is reset. (State 'C' of the channel selector is the 'stand by' state and comes 'on' only when the 'start' button is pressed).

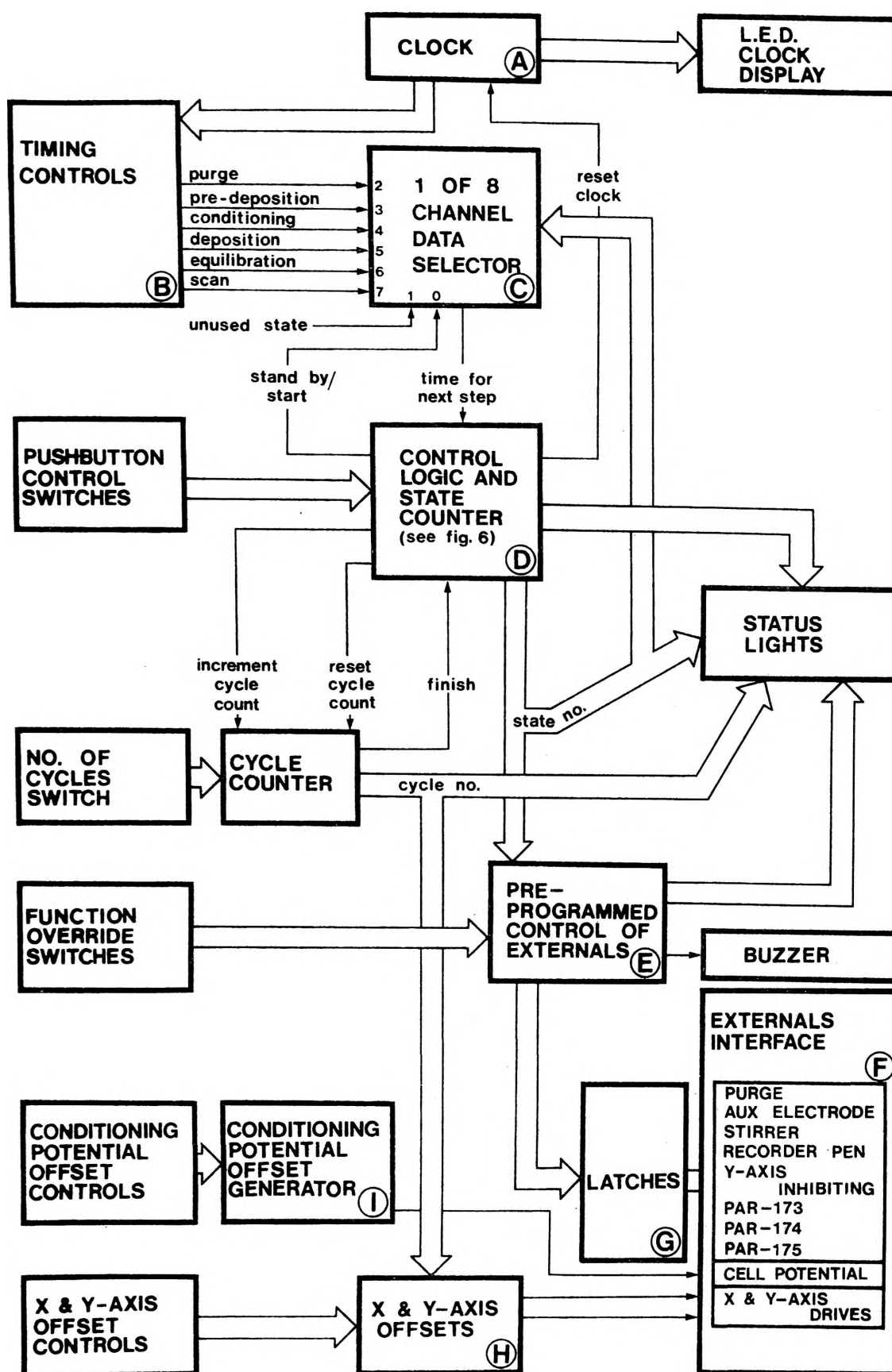


FIGURE 20 Simplified Schematic Overview of the Controller.

The *control logic and state counter* (D) governs which state the controller is in and effects changes in state as required by the timing, or when certain control switches are activated. As illustrated in Figure 21, the extensive use of J.K. flip flops throughout the control circuitry has allowed a great range of overriding controls. For example, the controller can be stepped manually through its entire analysis cycle if necessary.

The *pre-programmed control of externals* (E) uses a buffered diode gating circuit combined with overriding switches to 'decide' which externals are to be switched on in each state. The state of *peripheral equipment* (F) is electronically controlled within the controller using mechanical relays or CMOS I.C. switches according to the power requirements. I.C. *latches* (G) are employed to delay the external switches by differing amounts of time in order to 'smooth' the transition from one state to another.

The *X & Y-axis offsets* (H) are generated by digital to analogue converters working from the cycle number and the offset control switches. The *conditioning potential offset generator* (I) is basically a voltage reference source giving a positive or negative voltage as set by the front panel controls. The voltage created is buffered and fed to the potentiostat if required during conditioning.

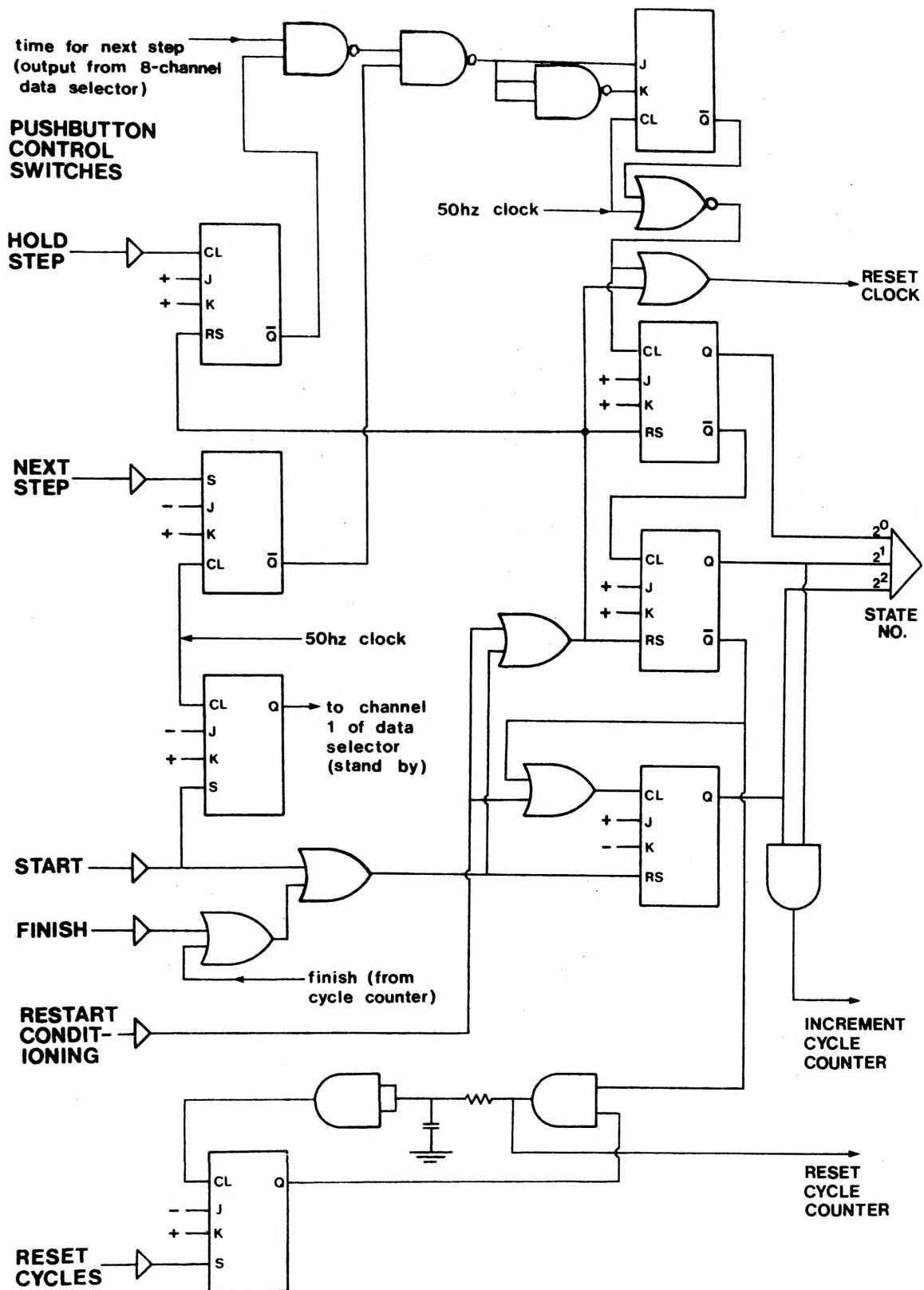


FIGURE 21 Control Logic and State Counter.

APPLICATION

The automatic controller prototype has completed in excess of 15,000 analysis cycles over 30 months of operation without any significant problems. All modes of controller operation have been thoroughly tested. Voltages applied to the cell from the potentiostat were examined closely with an oscilloscope but no voltage spikes from the switching operations associated with the controller were found.

The major application involved the development of the ASV methods for the analysis of Se(IV), Te(IV), As(III) and Sb(III) described in this work. The major advantages of automated operation were the excellent reproducibility of results, great versatility, and the extra time available for other laboratory work. The preparation of samples for analysis was carried out during, rather than between, the analyses. The daily number of samples analysed was almost doubled when the controller was put into operation.

Analysis of a sample comprises purging the solution followed by introduction of the electrode assembly into the solution and initiation of a further purge by the controller. The remainder of the analysis is completely automated with the operator being required only to make additions of standard solutions. During this work, the PAR-174 was used as a potentiostat and current to voltage converter while the PAR-175 was used to generate the required voltage ramps.

BIBLIOGRAPHY

BIBLIOGRAPHY

- ADAMIEC, I. & MARCZENKO, Z. (1975). Separation of microgram amounts of antimony by coprecipitation. *Chemia Analit.* 20, 985.
- ADAMS, R.N. (1962). Solid Electrodes. In P. Zuman and I.M. Kolthoff, 'Progress in Polarography' Vol. II (Interscience, New York).
- ADAMS R.N. (1969). Electrochemistry at Solid Electrodes. (Marcel Dekker, New York).
- ANALYTICAL METHODS COMMITTEE. (1975). The determination of small amounts of arsenic in organic matter. *Analyst*, 10, 54.
- ANDREWS, R.W. & JOHNSON, D.C. (1975). Voltammetric deposition and stripping of selenium(IV) at a rotating gold-disk electrode in 0.1 M perchloric acid. *Anal. Chem.* 47, 294.
- ANDREWS R.W. & JOHNSON D.C. (1976). Determination of selenium(IV) by anodic stripping voltammetry in flow system with ion exchange separation. *Anal. Chem.* 48, 1056.
- ARAKI, S., SUZUKI, S. & KUWABARA, T. (1973). Determination of tellurium(IV) and selenium(IV) by anodic stripping voltammetry using co-deposition with copper. *Japan Analyst*, 22, 700.
- A.S.T.M. (1969). Chemical Analysis of Metals. Sampling and Analysis of Metal Bearing Ores. (Philadelphia, Pa.).
- AZAD, J., KIRKBRIGHT, G.F. & SNOOK, R.D. (1979). Determination of selenium in oil digests by non-dispersive atomic-fluorescence spectrometry using an argon-hydrogen flame and the hydride generation technique. *Analyst*, 104, 232.
- BARNETT, W.B. & MCLAUGHLIN, E.A. JR. (1975). The atomic absorption determination of antimony, arsenic, bismuth, cadmium, lead and tin in iron, copper and zinc alloys with the graphite furnace. *Anal. Chim. Acta*, 80, 285.
- BATLEY, G.E. & FLORENCE, T.M. (1976). The effect of dissolved organics on the stripping voltammetry of seawater. *J. Electroanal. Chem.* 72, 121.
- BEDARD, M. & KERBYSON, J.D. (1976). Determination of arsenic, selenium, tellurium and tin in copper by hydride-evolution atomic-absorption spectrophotometry. *Can. J. Spectrosc.* 21, 64.
- BIGELOW, L.K. & CHEN, J.H. (1967). Effects of impurities on the annealability and resistivity of oxygen-bearing copper. *Met. Trans. B*, 7B, 661.

- BOND, A.M. (1975). Comparison of fundamental and second-harmonic A.C., and normal, derivative and differential pulse linear-sweep and stripping voltametric methods. *Anal. Chim. Acta*, 74, 163.
- BRAININA, KH.Z. (1974a). Stripping Voltammetry in Chemical Analysis. (Halsted Press, New York).
- BRAININA, KH.Z., NEIMAN, E.YA. & TRUKHACHEVA, L.N. (1971). Determination of antimony in copper and copper alloys by the method of inversion voltamperometry of ions of variable valence. *Ind. Lab.* 37, 19.
- BRAININA, KH.Z. & TCHERNYSHOVA, A.B. (1974). Inverse voltammetry of antimony with triphenylmethane dyes. *Talanta*, 21, 287.
- BREZONIK, P.L., BRAUNER, P.A. & STUMM, W. (1976). Trace metal analysis by anodic stripping voltammetry: effect of sorption by natural and model organic compounds. *Wat. Res.* 10, 605.
- BUDESINSKY, B.W. (1979). Arsenic colorimetry with silver diethyldithiocarbamate. *Microchem. J.* 24, 80.
- BULDINI, P.L. (1979). Polarographic evaluation of arsenic profiles in silicon. *Anal. Chim. Acta*, 106, 137.
- BURMISTROV, M.P., ZAKHAROV, Z.A., KIREEVA, N.P., MAKULOV, N.A. & ESSEN, A.I. (1976). Spectral analysis of high purity copper. *Ind. Lab.* 42, 1395.
- CARVALHO, M.B. & HERCULES, D.M. (1978). Trace arsenic determination by volatilization and x-ray photoelectron spectroscopy. *Anal. Chem.* 50, 2030.
- CASE, O.P. (1948). Photometric determination of arsenic in copper and copper-base alloys. *Anal. Chem.* 20, 902.
- CHAN, C.Y. & VIJAN, P.N. (1978). Semi-automated determination of antimony in rocks. *Anal. Chim. Acta*, 101, 33.
- CHEH, H.Y. & SARD, R. (1971). Electrochemical and structural aspects of gold electrodeposition from dilute solutions by direct current. *J. Electrochem. Soc.* 118, 1737.
- CHENG, K.L. (1961). Determination of traces of tellurium: bismuthiol II as a reagent for tellurium. *Talanta*, 8, 301.
- CLEM, R.G. & SCIAMANNA, A.F. (1975). Styrene impregnated, cobalt-60 irradiated, graphite electrode for anodic stripping analysis. *Anal. Chem.* 47, 276.
- COLLETT, D.L., FLEMING, D.E. & TAYLOR, G.A. (1978). Determination of antimony by stibine generation and atomic-absorption spectrophotometry using a flame-heated silica furnace. *Analyst*, 103, 1074.

- COPELAND, T.R., OSTERYOUNG, R.A. & SKOGERBOE R.K. (1974a). Elimination of copper-zinc intermetallic interferences in anodic stripping voltammetry. *Anal. Chem.* 46, 2093.
- COPELAND, T.R. & SKOGERBOE, R.K. (1974). Anodic stripping voltammetry. *Anal. Chem.* 46, 1257A.
- COUTSOURADIS, D., DIDERRICH, E., SMETS, J., CROCQ, G. & PAUWELS, L. (1974). Effect of trace amounts of impurities on the recrystallization behaviour of high-purity tough-pitch copper. *C.R.M. No. 39*, 73.
- CROW, D.R. (1979). *Principals and Applications of Electrochemistry*. 2nd Ed. (Halsted Press, New York).
- DAVIS, P.H., DULUDE, G.R., GRIFFIN, R.M., MATSON, W.R. & ZINK, E.W. (1978). Determination of total arsenic at the nanogram level by high-speed anodic stripping voltammetry. *Anal. Chem.* 50, 137.
- DIXON, K., RUSSELL, G.M., WALL, G. & EDDY, B.T. (1979). Analysis of anode slimes, especially copper slimes, by instrumental techniques. *Talanta*, 26, 833.
- DONALDSON, E.M. (1976). Spectrophotometric determination of tellurium in concentrates and brasses by chloroform extraction of the tellurium(IV) hexabromide-diantipryl-methane complex after separations by iron collection and xanthate extraction. *Talanta*, 23, 823.
- DONALDSON, E.M. (1977). Spectrophotometric determination of selenium in concentrates and high-purity copper metal with 3,3'-diaminobenzidine after separation by xanthate extraction. *Talanta*, 24, 441.
- DONALDSON, E.M. (1977a). Spectrophotometric determination of arsenic in concentrates and copper-base alloys by the molybdenum blue method after separations by iron collection and xanthate extraction. *Talanta*, 24, 105.
- DONALDSON, E.M. (1979). Determination of antimony in concentrates, ores and non-ferrous materials by atomic-absorption spectrophotometry after iron-lanthanum collection, or by the iodide method after further xanthate extraction. *Talanta*, 26, 999.
- ELLIOT, D.F., GLAZER, M. & RAMAKRISHNA, V. (1967). *Thermochemistry of Steel Smelting Processes*. Russian Translation. p. 132. (Metallurgiya, Moscow).
- EVANS, W.H., JACKSON, F.J. & DELLAR, D. (1979). Evaluation of a method for determination of total antimony, arsenic and tin in foodstuffs using measurement by atomic-absorption spectrophotometry with atomisation in a silica tube using the hydride generation technique. *Analyst*, 104, 16.

- FERRO, C.M., CALANDRA, A.J. & ARVIA, A.J. (1974). Volt-ammometric observations of the various stages related to the formation of electrochemical reduction of the anodic oxide layer on gold in acid aqueous solutions. *J. Electroanal. Chem.* 55, 291.
- FLATO, J.B. (1972). The renaissance of polarographic and voltammetric analysis. *Anal. Chem.* 44, 75A.
- FLORENCE, T.M. (1970). Anodic-stripping voltammetry with a glassy carbon electrode mercury-plated insitu. *J. Electroanal. Chem.* 27, 273.
- FORBES, S. & BOUND, G.P. (1977). Some investigations into the electroanalytical chemistry of selenium. *Proc. Analyt. Div. Chem. Soc.* 1977, 253.
- FORBES, S., BOUND, G.P. & WEST, T.S. (1979). Determination of selenium in soils and plants by differential pulse cathodic-stripping voltammetry. *Talanta*, 26, 473.
- FORSBERG, G., O'LAUGHLIN, J.W. & MEGARGLE, R.G. (1975). Determination of arsenic by anodic stripping voltammetry and differential pulse anodic stripping voltammetry. *Anal. Chem.* 47, 1586.
- FRANKE, J.P., DE ZEEUW, R.A. & HAKKERT, R. (1978). Evaluation and optimisation of the standard addition method for absorption spectrometry and anodic stripping voltammetry. *Anal. Chem.* 50, 1374.
- GALUS, E. (1976). *Fundamentals of Electroanalysis*. (E. Harwood, Chichester).
- GILLAIN, G., DUYCKAERTS, G. & DISTECHE, A. (1979). Direct and simultaneous determinations of zinc, cadmium, lead, copper, antimony and bismuth dissolved in sea water by differential pulse anodic stripping voltammetry with a hanging mercury drop electrode. *Anal. Chim. Acta*, 106, 23.
- GLADNEY, E.S., OWENS, J.W., MARPLE, M.L. & DREESEN, (1978). A comparison of thermal and epithermal neutron activation for the measurement of selenium in vegetation. *Anal. Lett.* 11, 1001.
- GREEN, T.E. & TURLEY, M. (1961). Selenium and Tellurium. In I.M. Kolthoff and P.J. Elving, 'Treatise on Analytical Chemistry'. Part II, Vol. 7. (Interscience, New York).
- GRIMANIS, A.P. & SOULIOTIS, A.G. (1967). Rapid determination of arsenic in copper and brass by neutron-activation analysis. *Analyst*, 92, 549.
- GRUNWALD, P., TSCHOPEL, P. & TOLG, G. (1976). Determination of low amounts of tellurium in copper and copper alloys

- with various methods of separation after coprecipitation with arsenic. *Z. Anal. Chem.* 279, 187.
- HAHN, R.B. (1978). Antimony. In I.M. Kolthoff and P.J. Elving, 'Treatise on Analytical Chemistry'. Part II, Vol. 10, p. 281. (Interscience, New York).
- HAMILTON, T.W. (1976). Anodic Stripping Voltammetry. Honours thesis, University of Wollongong.
- HAMILTON, T.W. (1976a). *Ibid.* Appendix II.
- HAMILTON, T.W., ELLIS, J. & HUNT, T.J. (1979). An automatic controller for voltammetric analysis. *Chem. Biomed. Environ. Instr.* 9, 353.
- HAMILTON, T.W., ELLIS, J. & FLORENCE, T.M. (1979a). Determination of selenium and tellurium in electrolytic copper by anodic stripping voltammetry at a gold film electrode. *Anal. Chim. Acta*, 110, 87.
- HAMILTON, T.W., ELLIS, J. & FLORENCE, T.M. (1980). Determination of arsenic and antimony in electrolytic copper by anodic stripping voltammetry at a gold film electrode. *Anal. Chim. Acta*, (in press).
- HANSEN, L.D., RICHTER, B.E., ROLLINS, D.K., LAMB, J.D. & EATOUGH, D.J. (1979). Determination of arsenic and sulfur species in environmental samples by ion chromatography. *Anal. Chem.* 51, 633.
- HEINEMAN, W.R. & KISSINGER, P.T. (1978). Analytical electrochemistry: methodology and applications of dynamic techniques. *Anal. Chem.* 50, 166R.
- HENRY, F.T., KIRCH, T.O. & THORPE, T.M. (1979). Determination of trace level arsenic(III), arsenic(V), and total inorganic arsenic by differential pulse polarography. *Anal. Chem.* 51, 215.
- HENRY, F.T. & THORPE, T.M. (1980). Determination of arsenic (III), arsenic(V) monomethylarsonate, and dimethylarsinate by differential pulse polarography after separation by ion exchange chromatography. *Anal. Chem.* 52, 80.
- HENZE, G., MONKS, P., TOLG, G., UMLAND, F. & WEBLING, E. (1969). On the simultaneous determination of selenium and tellurium in the low ppb-range by cathodic stripping voltammetry. *Z. Anal. Chem.* 295, 1.
- HOEDE, D. & VAN DER SLOOT, H.A. (1979). Application of hydride generation for the determination of antimony and arsenic in biological material by neutron activation analysis. *Anal. Chim. Acta*, 111, 321.
- JAGNER, D. & GRANELL, A. (1976). Potentiometric stripping analysis. *Anal. Chim. Acta*, 83, 19.

- JEDRZEJEWSKA, H. (1973). Determination of tellurium in conductor-grade and vacuum-refined copper by atomic-absorption spectrophotometry. *Chemia Analit.* 18, 117.
- KAMENEV, A.I., VINOGRADOVA, E.N. & RUSSY, A.T. (1973). Polarographic determination of low tellurium(IV) concentrations. *J. Anal. Chem. USSR*, 28, 619.
- KINNUNEN, J. & LUOMA, J. (1978). Separation of selenium for its determination in metallurgical products. 2. *Anal. Chem.* 291, 221.
- KISSINGER, P.T. (1974). Analytical electrochemistry: methodology and applications of dynamic techniques. *Anal. Chem.* 46, 15R.
- KISSINGER, P.T. (1976). Analytical electrochemistry: methodology and applications of dynamic techniques. *Anal. Chem.* 48, 17R.
- KOPANICA, M. & STARA, V. (1979). Differential pulse polarographic determination of tellurium. Application of catalytic hydrogen current. *J. Electroanal. Chem.* 98, 213.
- KRAPIVKINA, T.A., ROIZENBLAT, E.M. & KALAMBET, G.A. (1975). Determination of selenium by inversion voltammetry at graphite electrode. *Ind. Lab.* 41, 317.
- KUWABARA, T., SUZUKI, S. & ARAKI, S. (1973). Determination of arsenic(III) by anodic stripping method using co-deposition with copper. *Bull. Chem. Soc. Japan*, 46, 1690.
- LOUCKA T. (1973). The adsorption, oxidation and reduction of arsenious acid on gold and platinum electrodes. *J. Electroanal. Chem.* 47, 103.
- LUCKE, K. & DETERT, K. (1957). *Acta Met.* 5, 628. (Original not seen).
- LUKE, C.L. (1959). Photometric determination of traces of selenium or tellurium in lead or copper. *Anal. Chem.* 31, 572.
- MCDANIEL, M., SHENDRIKAV, A.D., REISZNER, K.D. & WEST, P.W. (1976). Concentration and determination of selenium from environmental samples. *Anal. Chem.* 48, 2240.
- MACKAY, K.E. & ARMSTRONG SMITH, G. (1966). Quality control of electrolytic tough pitch copper. *Trans. Inst. Min. Met., Sect. C*, 75, 269.
- MAIENTHAL, E.J. & TAYLOR, J.K. (1965). Determination of tellurium by cathode-ray polarography. *Anal. Chem.* 37, 1516.

- MEYER, A., GRALLATH, E., KAISER, G. & TOELG, G. (1976). Extremely sensitive method of determination of selenium by gas chromatography after separation by evaporation in a stream of oxygen I. Determination in high-purity copper. *Z. Anal. Chem.* 281, 201.
- MONTASER, A. & MORTAZAVI, J. (1980). Optical emission spectrometry with an inductively coupled plasma operated in argon-nitrogen atmosphere. *Anal. Chem.* 52, 255.
- MOTT, N.F. & JONES, H. (1958). *The Theory of the Properties of Metals and Alloys.* (Dover, New York).
- MULLEN, J.D. (1976). The determination of selenium and other impurities in high-purity copper by flameless atomic-absorption spectrophotometry. *Talanta*, 23, 846.
- MULLEN, J.D. (1977). Determination of arsenic in high purity copper by flameless atomic-absorption spectrophotometry. *Talanta*, 24, 657.
- NAKAHARA, T., KOBAYASHI, S. & MUSA, S. (1979). The determination of trace amounts of arsenic in waste-waters by non-dispersive atomic fluorescence spectrometry after hydride generation. *Anal. Chim. Acta*, 104, 173.
- NAKASHIMA, S. (1979). Selective determination of arsenic (III) and arsenic(V) by atomic-adsorption spectrophotometry following arsine generation. *Analyst*, 104, 172.
- NAZARENKO, I.I. & KISLOVA, I.V. (1978). Determination of different forms of selenium in water. *J. Anal. Chem. USSR*, 33, 1429.
- NEEB, R. & KIEHNAST, I. (1970). Electrochemical masking in inverse voltammetry. *Naturwissen.* 57, 37.
- NEIMAN, E.YA., DOLGOPOLOVA, G.M., TRUKHACHEVA, L.N. & DMITRIEV, K.G. (1970). Determination of antimony and Bismuth in high-purity copper by film polarography with accumulation. *Ind. Lab.* 36, 821.
- NEIMAN, E.YA. & DOLGOPOLOVA, G.M. (1975). Stripping-voltammetric determination of selenium and tellurium in high-purity copper. *Ind. Lab.* 41, 651.
- NEIMAN, E.YA., FIGEL'SON, YU.A. & YAKOVLEVA, V.G. (1975a). Stripping-voltammetric study of the conditions for the electrodeposition of tellurium on various graphite electrodes. *J. Anal. Chem. USSR*, 30, 1666.
- NEIMAN, E.YA., PETROVA, L.G., IGNATOV, V.I. & DOLGOPOLOVA G.M. (1980). The third element effect in anodic stripping voltammetry. *Anal. Chim. Acta*, 113, 277.
- NEIMAN, E.YA. & SUMENKOVA, M.F. (1976). Simultaneous determination of antimony and gold by stripping voltammetry. *J. Anal. Chem. USSR*, 31, 741.

- NEIMAN, E.YA. & SUMENKOVA, M.F. (1977). Determination of antimony and copper in copper-alloys by method of inverse voltamperometry. *Ind. Lab.* 43, 481.
- NEIMAN, E.YA. & TRUKHACHEVA, L.N. (1972). Determination of impurities in high-purity copper by inversion voltammetry. *Ind. Lab.* 38, 1551.
- NGHI, T.V. & VYDRA, F. (1975). Voltammetry and electrochemical stripping analysis for antimony in aqueous and non-aqueous media after extraction. *Anal. Chim. Acta*, 80, 267.
- PAHLAVANPOUR, B., PULLEN, J.H. & THOMPSON, M. (1980). Determination of trace concentrations of selenium in soils and sediments by the introduction of hydrogen selenide into an inductively coupled plasma source for emission spectrometry. *Analyst*, 105, 274.
- PAKALNS, P. (1969). Spectrophotometric determination of traces of arsenic by an extraction method. *Anal. Chim. Acta*, 47, 225.
- PERONE, S.P. & BIRK, J.R. (1965). Application of derivative techniques to anodic stripping voltammetry. *Anal. Chem.* 37, 9.
- REESE, D.A. & CONDRA, L.W. (1969). Impurities in copper wirebars. *Wire Ind.* 1969, 883.
- REICHEL, W. & BLEAKLEY, B.G. (1974). Concentration and determination of trace impurities in copper by atomic-absorption spectrophotometry. *Anal. Chem.* 46, 59.
- RENGAN, K., HAUSHALTER, J.P. & JONES, J.D. (1979). Simultaneous determination of arsenic and antimony in environmental samples by radiochemical neutron activation analysis. *J. Radioanalytical Chem.* 54, 347.
- RIFKIN, S.C. & EVANS, D.H. (1976). General equation for voltammetry with step-functional potential changes applied to differential pulse voltammetry. *Anal. Chem.* 48, 1616.
- ROBINS, W.B. & CARUSO, J.A. (1979). Determination of germanium, arsenic, selenium, tin and antimony in complex samples by hydride generation - microwave-induced plasma atomic-emission spectrometry. *Analyst*, 104, 35.
- ROSENFELD, I. & BEATH, D.A. (1964). *Selenium*. 2nd Ed. (Academic Press, New York).
- SHAFIQU ALAM, A.M., VITTORI, D. & PORTHAULT, M. (1976). Determination of selenium(IV) in acid solutions with A.C. polarography and differential pulse polarography. *Anal. Chim. Acta*, 87, 437.

- SHIMOISHI, Y. (1975). Gas-chromatographic determination of selenium in copper metal and copper salts with 4-nitro-o-phenylenediamine. *Bull. Chem. Soc. Japan*, 48, 2797.
- SIEMER, D.D. & KOTEEL, P. (1977). Comparisons of methods of hydride generation atomic absorption spectrometric arsenic and selenium determination. *Anal. Chem.* 49, 1096.
- SKOGERBOE, R.K. & BEJMUK, A.P. (1977). Simultaneous determination of arsenic, germanium, and antimony by gas chromatography after hydride generation. *Anal. Chim. Acta*, 94, 297.
- SKONIECZNY, R.F. & HAHN, R.B. (1978). Arsenic. In I.M. Kolthoff and P.J. Elving, 'Treatise on Analytical Chemistry'. Part II, Vol.10, p. 210. (Interscience, New York).
- SMITH, A.E. (1975). Interferences in the determination of elements that form volatile hydrides with sodium borohydride using atomic-absorption spectrophotometry and the argon-hydrogen flame. *Analyst*, 100, 300.
- SNEED, M.C., MAYNARD, J.L. & BRASTED, R.C. (1954). Comprehensive Inorganic Chemistry. Vol. II, p. 107. (D. Van Nostrand, New York).
- STOJEK, Z., STEPNIK, B. & KUBLIK, Z. (1976). Cyclic and stripping voltammetry with graphite based thin mercury film electrodes prepared insitu. *J. Electroanal. Chem.* 74, 277.
- STULIKOVA, M. (1973). The deposition and stripping of mercury on a glassy carbon rotating disk electrode. *J. Electroanal. Chem.* 48, 33.
- STULIKOVA, M. & STULIK, K. (1974). Utilization of hydrocarbon materials in electroanalytical chemistry. *Chem. Listy*, 68, 800.
- TALMI, Y. & BOSTICK, D.T. (1975). Determination of alkyl-arsenic acids in pesticide and environmental samples by gas chromatography with a microwave emission spectrometric detection system. *Anal. Chem.* 47, 2145.
- TERADA, K., OKUDA, K., MAEDA, K. & TIBA, T. (1978). A neutron activation analysis of selenium, arsenic and antimony in rocks and sediments by simultaneous evolution with bromide-strong phosphoric acid reagent. *J. Radioanal. Chem.* 46, 217.
- THOMPSON, K.C. (1975). The atomic-fluorescence determination of antimony, arsenic, selenium and tellurium by using the hydride generation technique. *Analyst*, 100, 307.

- THOMPSON, M., PAHLAVANPOUR, B., WALTON, S.J. & KIRKBRIGHT, G.F. (1978). Simultaneous determination of trace concentrations of arsenic, antimony, bismuth, selenium and tellurium in aqueous solution by introduction of the gaseous hydrides into an inductively coupled plasma source for emission spectrometry. Part II. Interference studies. *Analyst*, 103, 705.
- THOMPSON, M., PAHLAVANPOUR, B., WALTON, S.J. & KIRKBRIGHT, G.F. (1978a). Simultaneous determination of trace concentrations of arsenic, antimony, bismuth, selenium and tellurium in aqueous solution by introduction of the gaseous hydrides into an inductively coupled plasma source for emission spectrometry. Part I. Preliminary studies. *Analyst*, 103, 568.
- THOMPSON, K.C. & THOMERSON, D.R. (1974). Atomic-absorption studies on the determination of antimony, arsenic, bismuth, germanium, lead, selenium, tellurium and tin by utilizing the generation of covalent hydrides. *Analyst*, 99, 595.
- TOPANICA, M. & STARA, V. (1978). Anodic stripping voltammetry of tellurium(IV) in aqueous solution and mixed solvents. *J. Electroanal. Chem.* 91, 351.
- UNDERKOFER, W.L. & SHAIN, I. (1965) Investigation of A.C. polarography at stationary electrodes, with application to stripping analysis. *Anal. Chem.* 37, 218.
- VAJDA, F. (1970). Stripping voltammetry of Se(IV) Compounds with the hanging mercury drop electrode. *Acta. Chim. Acad. Sci. Hung.* 63, 257.
- VAN DYKE, G. & VERBECK, F. (1973). Determination of traces of antimony and tin in copper. *Anal. Chim. Acta.* 66, 251.
- VASSOS, B.H., BERLANDI, F.J., NEAL, T.E. & MARK, H.B. (1965). Electrochemical preparation of thin metal films as standards on pyrolytic graphite. *Anal. Chem.* 37, 1653.
- VASSOS, B.H. & MARK, H.B. JR. (1967). Anodic dissolution of thin films of copper metal from pyrolytic graphite - a study of multiple dissolution current peaks. *J. Electroanal. Chem.* 13, 1.
- VIJAYAKUMAR, M., RAMAKRISHNA, T.V. & ARAVAMUDAN, G. (1979). Spectrophotometric determination of tellurium in trace quantities by use of an ion-association complex. *Talanta*, 26, 323.
- VOLAIRE, M., VITTORI, O. & PORTHAULT, M. (1974). Determination of tellurium(IV) in acid solution by pulse polarography and linear sweep voltammetry. *Anal. Chim. Acta.* 71, 185.

- VYDRA, F. (1976a). Electrochemical stripping on rotating disk-electrode from glassy carbon. *Chem. Listy*, 70, 337.
- VYDRA, F., STULIK, K. & JULAKOVA, E. (1976). Electrochemical Stripping Analysis. (Halsted Press, New York).
- WHITNACK, G.C. & BROPHY, R.G. (1969). A rapid and highly sensitive single-sweep polarographic method of analysis for arsenic(III) in drinking water. *Anal. Chim. Acta*, 48, 123.
- YADAV, A.A. & KHOPKAR, S.M. (1971). Rapid extraction of antimony with tributyl phosphate. Direct photometric determination with brilliant green. *Bull. Chem. Soc. Japan*, 44, 693.
- ZAKHARCHUK, N.F., YUDELEVICH, I.G. & CHERNOV, S.V. (1975). Inverse (stripping) voltammetry of tellurium in a thin layer of solution. *J. Anal. Chem. USSR*, 30, 1201.
- ZELYANSKAYA, A.I., BYKOV, I.E. & GORSHKOVA, L.S. (1957). Separation of selenium and tellurium by the use of a cation exchanger. *Trudy Inst. Met. Ural. Filial Akad. Nauk SSSR*, 1957, 151; *Referat. Zhur. Khim.* 1958. *Chem. Abs.* 53, 6719d.
- ZOT'EVA, T.A. (1973). Determination of arsenic impurities in acid copperplating baths. (Exchange of experience). *Ind. Lab.* 39, 1258.

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